On the Sign of the ^{119}Sn Quadrupole Interaction in the Mössbauer Spectra of Me_2SnCl_2, Me_2SnMoO_4, and SnO_2

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Summary Previously reported conclusions regarding the nature of the charge distribution about ^{119}Sn in Me_2SnCl_2 and Me_2SnMoO_4 are shown to be in error; the claim that ΔE for ^{119}Sn in SnO_2 is $\leqslant 0{\cdot}2$ mm/sec is unwarranted.

IN a recent communication Goodman and Greenwood[1] reported the Mössbauer spectra of three polycrystalline tin compounds subjected to strong external magnetic fields applied perpendicular to the direction of observation of the γ-beam. Two of the materials studied, Me_2SnCl_2 and Me_2SnMoO_4, had substantial quadrupole splittings, ΔE, of 3·4 and 4·2 mm/sec, respectively, and one object of their study was the determination of the sign of the ^{119}Sn quadrupole coupling constant, e^2qQ, in these compounds, both of which, they assumed, possessed *trans*-octahedral R_2SnX_4 structures. Using a very simplified† energy-level diagram constructed to show the combined effects of a simultaneous quadrupole and externally applied magnetic interaction, they concluded that in both compounds the external charge distribution was such that there was an excess of negative charge in the SnX_4 plane over that along the Me–Sn–Me bond direction.

This conclusion is in contradiction to previously reported studies[2] of the systematics of electric charge distributions about tin in a variety of compounds. In two compounds which are known from *X*-ray studies to possess *trans*-R_2SnX_4 structures, Me_2SnF_2[3] and $Me_2Sn(C_5H_7O_2)_2$,[4] the external charge distribution corresponds to an excess of electron density along the Me–Sn–Me bond axis provided that the sign of the nuclear quadrupole moment, Q, is negative as reported by Boyle, Bunbury, and Edwards.[5] Further, for Me_2SnCl_2, Mössbauer spectra obtained with the compound subjected to an external magnetic field applied parallel to the γ-beam indicated[2] that while $(V_{zz})_0$ was negative, the asymmetry parameter, η, was neither zero nor unity indicating that the molecular geometry in the solid was neither octahedral nor tetrahedral. The intermediate value of η of *ca.* 0·6 (η can only vary between 0 and 1) was interpreted as indicating that the Me–Sn–Me bond angle was greater than the ideal tetrahedral angle but much less than 180°. It has since come to our attention that *X*-ray studies have indeed indicated that such an increase in bond angle does occur[6] in Me_2SnCl_2.

This contradiction led us to suspect that either the energy level diagram used in ref. 1 was too oversimplified and/or there was an error in the assigned charge distribution. Indeed, the authors stated that both $(V_{zz})_0$ and the electric field gradient along the z direction, E_{zz}, were positive in these compounds, which is impossible since $(V_{zz})_0 \equiv eq = -E_{zz}$. To check on these possibilities, exact calculations of the expected Mössbauer spectra were performed for the experimental parameters given in ref. 1 using a version of the program PDRHXT[7] which had been modified to handle a transverse geometry. The results of these calculations, shown in Figures 1 and 2 as both line and Lorentzian spectra, are plotted as absorption instead of transmission spectra as in ref. 1. Comparison of these curves with those in Fig. 2 of ref. 1 shows very good agreement for Me_2SnMoO_4 assuming that $\eta \approx 0$ and that positive velocity increases to the right side of the curves in both Figures. For Me_2SnCl_2, one seems to get the best agreement for a value of η of *ca.* 0·6, in rough agreement

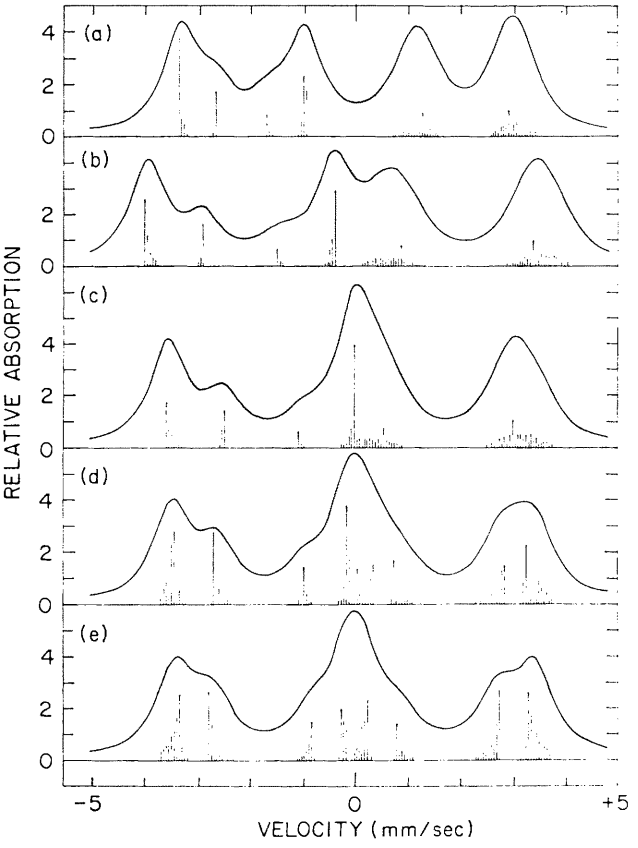

FIGURE 1. ^{119}Sn *Mössbauer line and Lorentzian absorption spectra for isotropic samples in transverse magnetic fields*;
(a) $\Delta E = 4{\cdot}2$ mm/sec, $\eta = 0$, $H = 20$ kgauss
(b) $\Delta E = 4{\cdot}2$ mm/sec, $\eta = 0$, $H = 30$ kgauss
(c) $\Delta E = 3{\cdot}4$ mm/sec, $\eta = 0$, $H = 30$ kgauss
(d) $\Delta E = 3{\cdot}4$ mm/sec, $\eta = 0{\cdot}6$, $H = 30$ kgauss
(e) $\Delta E = 3{\cdot}4$ mm/sec, $\eta = 1{\cdot}0$, $H = 30$ kgauss
In all cases, e^2qQ *is positive and the full linewidth,* 2Γ, *for the Lorentzian spectra is* 0·8 *mm/sec.*

† The energy level diagram shown in Figure 1 (ii) of ref. 1 is "valid" for only one orientation of the magnetic field, H, and the electric field gradient, E_{kk}, tensor systems and cannot be taken to represent the splittings expected for an isotropic sample where an appropriate average over all orientations is required. Further, since the energy of a nuclear magnetic sublevel, $E(m_I)$, in the absence of a quadrupole interaction is proportional to $-\mu m_I H$ where μ is the magnetic moment of the appropriate nuclear state with spin I, the signs of all the m_I levels shown in Figure 1 (i) [and probably also of Figure 1 (ii)] of ref. 1 should be reversed.

with previous results. A precise determination of η is difficult, however, since it requires a more detailed comparison of calculated and experimental spectra than is possible with the spectra as presented.

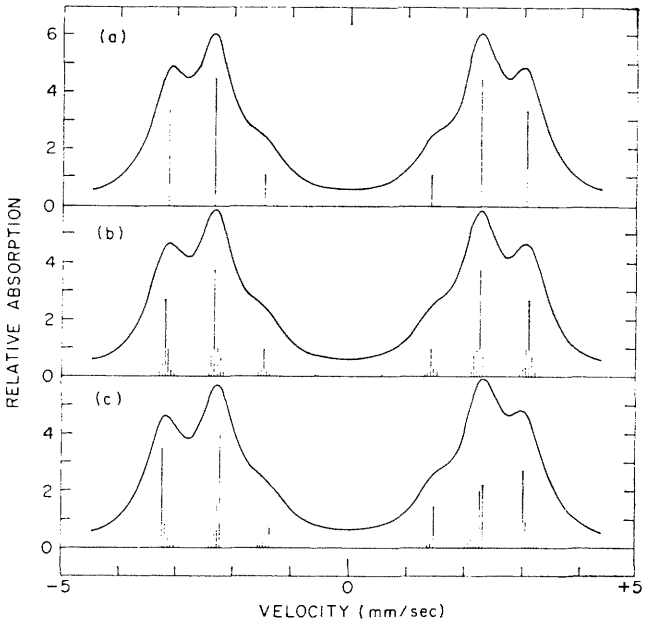

FIGURE 2. ^{119}Sn *Mössbauer line and Lorentzian absorption spectra for isotropic samples in a transverse magnetic field of* 45 *kgauss*;
(a) $\Delta E = 0$, $\eta = 0$
(b) $\Delta E = 0{\cdot}36$ mm/sec, $\eta = 1{\cdot}0$
(c) $\Delta E = 0{\cdot}36$ mm/sec, $\eta = 0{\cdot}0$
In all cases where $\eta = 0$, e^2qQ *is positive and the full linewidth,* 2Γ, *for the Lorentzian spectra is* 0·8 *mm/sec.*

In brief, the sign of $(V_{zz})_0$ would appear to be negative in both of these compounds while the small or vanishing value of η in Me_2SnMoO_4 suggests that Me–Sn–Me bond must be nearly linear. As reported previously,[2] the negative sign of $(V_{zz})_0$ [which corresponds to an excess of negative charge along the z axis] in *trans*-R_2SnX_4 compounds is most logically interpreted by assuming that tin–carbon bonds have a much larger effective p-electron density located on the tin along this bond axis than do tin–halide or tin–oxygen or –chalcogen bonds along their bond axes.

Goodman and Greenwood also reported the Mössbauer spectrum of SnO_2 subjected to an external field of 45 kgauss. They concluded that since the observed pattern was nearly symmetrical, any quadrupole interaction in this compound must be $\leqslant 0{\cdot}2$ mm/sec. This is quite surprising since there has been considerable discussion[8] about not only the magnitude (variously reported as being between 0·25 and 0·55 mm/sec) but also the origin, of the quadrupole interaction found in at least some samples of SnO_2. Unfortunately they failed to recognize that the immediate geometry about the tin in SnO_2 virtually requires that η be very large. When $\eta = 1$, the Mössbauer spectrum of a truly isotropic sample of a 3/2–1/2 nuclear spin state Mössbauer isotope such as ^{57}Fe or ^{119}Sn subjected to an external magnetic field is expected to be symmetrical about the centre of the two original quadrupole lines. This is shown in Figures 1(e) and 2(b) for quadrupole splittings of 3·4 and 0·36 mm/sec. For small quadrupole splittings and large asymmetry parameters, the resultant pattern will superficially appear to be that of a simple magnetic spectrum with no quadrupole interaction [compare Figures 2(a) and 2(b)] and a careful comparison of calculated and observed spectral chracteristics is required to determine whether the original "single" line was indeed single or an overlap of two closely spaced quadrupole split lines. The detail in the published spectrum is not sufficient to enable us to make such a comparison but the claim that ΔE in SnO_2 is $\leqslant 0{\cdot}2$ mm/sec is unwarranted.

After this manuscript was completed, the authors of ref. 1 acknowledged[9] that the sign convention they used for V_{zz} was in error.

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