The Sign of the Quadrupole Interaction in Some Tin(II) Compounds

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Summary. The signs of the quadrupole coupling constants, e^2qQ, in the compounds SnF_2, SnO, SnS, $Sn_3(PO_4)_2$, and SnC_2O_4 have been determined to resolve inconsistencies in the literature, and all have a positive value, implying that the dominant contribution to the electric-field gradient arises from the p_z electron density in the non-bonding orbital.

SEVERAL papers have been published on the interpretation of quadrupole splittings in Sn^{II} compounds.[1-4] Lees and Flinn[2,3] obtained plots of the chemical isomer shift, δ, against the quadrupole splitting, Δ, and found that most of the compounds they studied fell close to one of two straight lines whose slopes differed by a factor of 2. The quadrupole splitting was then interpreted as arising from p_z electron density on the tin in one case and from $p_{x,y}$ electron density in the other case. The few compounds which fell between these lines were assigned a mixture of $p_{x,y}$ and p_z character.

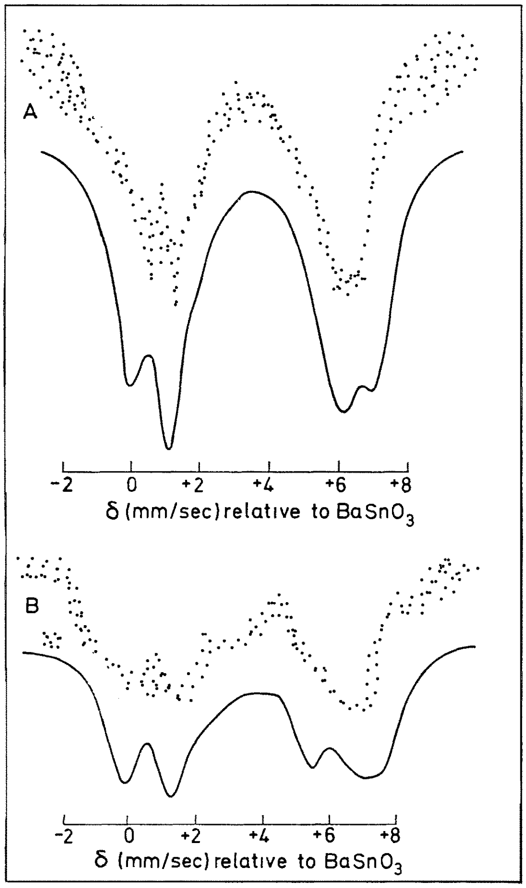

FIGURE. *Experimental and computed line shapes.*
(A) SnS. $H_{\perp} = 50$ kG. $\Delta = +1.0$ mm./sec., $\Gamma = 0.9$ mm./sec., $\eta = 0$. (B) SnC_2O_4. $H_{\perp} = 50$ kG, $\Delta = +1.8$ mm./sec., $\Gamma = 1.0$mm./sec. $\eta = 0$.

According to this graph, tetragonal tin(II) oxide (SnO) has an excess of $p_{x,y}$ character, in direct contrast to the work of Boyle *et al.*[5] where the quadrupole splitting was taken as arising predominantly from p_z electron density.

Donaldson and Senior[4] have calculated $p_{x,y}$ and p_z orbital occupation for a number of tin(II) compounds in which the tin is co-ordinated to three other atoms. Again, a linear relationship between isomer shift and quadrupole splitting was obtained. However, SnF_2 was calculated to have more electron density in each of p_x and p_y than in p_z. On the other hand SnS was considered to have more p_z than $p_{x,y}$ character. In direct contrast with these deductions, Lees and Flinn predicted that SnF_2 should have mainly p_z and SnS mainly $p_{x,y}$ electron density.

It was this ambiguity in the interpretation of the quadrupole splitting in Sn^{II} Mossbauer spectra that led us to carry out the present work on the determination of the sign of the quadrupole coupling constant, e^2qQ, for selected compounds. By the application of a large magnetic field a combined magnetic and quadrupole interaction is obtained.[6] With the magnetic field which can be obtained by means of a conventional superconducting magnet, *i.e. ca.* 50kG, these interactions are of the same order of magnitude for most compounds of interest. Hence the spectra are frequently not interpretable by simple inspection. However, by using the programme of Gibb,[7] curves can be computed, using the known values for the field and quadrupole splitting, which correspond very closely to those observed experimentally. The Figure illustrates the experimental data and computed line shapes for tin(II) sulphide and oxalate which are representative of the results obtained in this work. They were obtained with the magnetic field perpendicular to the direction of the γ-rays.

Solution of the quadrupolar Hamiltonian for ^{119}Sn gives $\Delta = \frac{1}{2}|e^2qQ|[1 + (\eta^2/3)]^{\frac{1}{2}}$ where η is the asymmetry parameter. If η is less than 0.5 it has no significant effect on the spectrum,[7] and can be ignored for the present purposes. If the sign of Q is taken to be negative[5] then the sign of eq, which relates to the chemical bonding,[8] can be obtained by determining the sign of e^2qQ. Hence, using the known values of eq for various orbitals it is possible to interpret the quadrupole interaction in terms of an excess of electron density in one set of orbitals over the other. In these expressions e is the charge on the proton, in our earlier communication[6] we erroneously used the opposite sign convention. Hence for negative Q, e^2qQ is positive for p_z, d_{z^2}, d_{xz}, and d_{yz} and negative for p_x, p_y, $d_{x^2-y^2}$ and d_{xy}.

The compounds studied in the present work were tin(II) fluoride, oxide, sulphide, orthophosphate [$Sn_3(PO_4)_2$], and oxalate. All are found to have positive values for e^2qQ. This agrees with the assignment of e^2qQ for SnO by Boyle *et al.*[5] but disagrees with the conclusions of Lees and Flinn[2] for SnO and SnS and the calculations of Donaldson and Senior[4] for SnF_2.

Since the calculations of Greenwood *et al.*[9] have shown that the $5d$-electrons make only a small contribution to the quadrupole splitting in Sn^{IV} compounds, it is reasonable to interpret the *sign* of e^2qQ in these Sn^{II} compounds in terms of p-electron density, bearing in mind that the *magnitude* will be influenced to some extent by the participation of the tin d-orbitals in the bonding. In each case an excess of p_z electron density over $p_{x,y}$ is indicated. This excess is probably produced by the effect of the lone pair of electrons in Sn^{II}, which can have appreciable p_z character since the orbital lies along the z-axis of the structure.

In the five Sn^{II} compounds we have studied, the dominant contribution to the electric-field gradient arises from the p_z electron density in the non-bonding orbital.

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