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Determination of the sign of the quadrupole coupling constant (e^2qQ) of Sn^{2+} in silicate glasses by Mössbauer spectroscopy

P G Appleyard[†], J A Johnson[†], C E Johnson[‡], M F Thomas[‡], D Holland[§] and A Sears[§]

[†] School of the Built Environment, John Moores University, Liverpool L3 5UG, UK

[‡] Department of Physics, University of Liverpool, Liverpool L69 3BX, UK

[§] Department of Physics, University of Warwick, Coventry CV4 7AL, UK

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Abstract. High-field ^{119}Sn Mössbauer spectroscopy was performed on a range of tin-containing ternary and binary silicate glass systems. All the glasses unambiguously exhibited a positive value for e^2qQ for the Sn^{2+} valence state. Determination of the sign of e^2qQ indicates that the electron distribution around each Sn nucleus is similar at all the tin atoms, which is a significant finding for glasses. These results suggest that the electronic state of the Sn^{2+} is dictated by its non-bonding electron orbital, which has strong p_z character, and which provides the dominant contribution to the electric field gradient present at the ^{119}Sn nucleus.

1. Introduction

Mössbauer studies give information on the local electron distribution about the Mössbauer nucleus. In glasses, the question arises of whether this distribution for a particular constituent atom is similar at all sites or is random. The shape of the electron distribution may be determined from measurements of the electric quadrupole splitting. In particular the magnitude of the electric field gradient (EFG) is proportional to the deviation of the departure of the distribution from spherical symmetry, while the sign indicates the sense (elongated or compressed) of the distortion.

Using ^{119}Sn Mössbauer spectroscopy on tin atoms in glasses, we have observed the mean magnitude of the interaction between the quadrupole moment of the Sn nucleus and the EFG. This quadrupole interaction has a sign that is normally inaccessible as the two transitions involved have equal intensity, due to the random orientation of the EFG principal axis to the γ -ray direction.

Tin silicate glasses do not possess an internal magnetic field. However, application of an external magnetic field will give rise to a combined magnetic interaction and quadrupole interaction which is sensitive to the sign of the latter. The feasibility of using this technique to determine the sign of e^2qQ in randomly orientated polycrystalline powders is well documented. Collins [1] illustrated how such a method may be employed to characterize e^2qQ (the quadrupole coupling constant) and η (asymmetry parameter, $(V_{xx} - V_{yy})/V_{zz}$) in polycrystalline ferrocene where a large applied field acted as a perturbation on the quadrupole splitting of the ^{57}Fe resonance. Gibb *et al* [2] successfully determined the sign of e^2qQ

in Sn^{2+} compounds SnF_2 , SnO , SnS , $\text{Sn}_3(\text{PO}_4)_2$ and SnC_2O_4 to be positive. However the technique has not been previously used on tin-containing glasses.

The Hamiltonian [3] describing the interaction between EFG, applied magnetic field and nucleus is given by

$$H = -g\mu_N \hat{I} \cdot \mathbf{B} + \frac{e^2 q Q}{4I(2I-1)} [3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2}(\hat{I}_+^2 + \hat{I}_-^2)] \quad (1)$$

where g is the nuclear g -factor, μ_N is the nuclear magneton, \mathbf{B} is the applied magnetic field, \mathbf{I} is the spin operator acting along the Zeeman quantization axis, \hat{I}_z is the spin operator acting on the z axis of the EFG co-ordinate system and \hat{I}_+ and \hat{I}_- are raising and lowering operators. q is the magnitude of the EFG and Q is the quadrupole moment of the nucleus, which for ^{119}Sn is ~ -0.08 barn. The excited state has spin $+\frac{3}{2}$.

The energy levels for such a combined magnetic and quadrupole interaction may only be calculated in closed form for a few special cases. For non-magnetic ^{119}Sn samples in an applied laboratory field, the magnitude of $g\mu_N \mathbf{I} \cdot \mathbf{B}$ is comparable to $e^2 q Q$, making a perturbation treatment invalid. In such a case there is no closed-form solution [4] and the energy levels may only be determined by solving (1) exactly.

2. Experiment

2.1. The glass samples

The investigation was performed on a range of ternary and binary silicate glass systems. The glasses chosen included $\text{K}_2\text{O}:\text{SiO}_2:\text{SnO}$ (sample 1), $\text{Na}_2\text{O}:\text{SiO}_2:\text{SnO}$ (samples 2 and 3), $\text{Li}_2\text{O}:\text{SiO}_2:\text{SnO}$ (sample 6) and $\text{Rb}_2\text{O}:\text{SiO}_2:\text{SnO}$ (sample 7) ternary systems and a $\text{SiO}_2:\text{SnO}$ (sample 5) binary [6] system. A doped float glass sample [5] (sample 4) prepared by Warwick University, to emulate in bulk the compositional properties found in the surface of commercial float glass manufactured by Pilkington, was also examined.

The samples were prepared from the stoichiometric quantities of the chemical concerned i.e. alkali metal carbonates, quartz SiO_2 and stannous oxalate. The powders were mixed together and the mixture formed into pellets which were then heated to the required melting temperature in a silica crucible which was placed in an outer crucible with a lid such that a CO_2 rich atmosphere was produced. The crucibles were removed from the furnace after approximately 1 h and allowed to cool to 400°C in air before transfer to an annealing furnace, holding for 1 h and then slow cooling to room temperature. The resulting glass was cut from the crucible. Chemical analysis[†] was used to determine element ratios and the relative amount of the tin oxidation states. The actual compositions of all the samples are listed in table 1.

From the table it is seen that all of the primarily SnO -containing glasses also possess minor amounts of SnO_2 . However, of these glasses, only sample 3 was fitted incorporating a component for the Sn^{4+} . An exception to this was the float glass sample (sample 4), containing only Sn^{4+} , which was fitted with a single component.

2.2. Mössbauer spectroscopy

Powder samples of calculated optimum thickness [7] were made and placed in cylindrical sample holders of 13 mm diameter and 1 mm thickness. The source was of ^{119}Sn in a matrix

[†] Courtesy of Pilkingtons Glass PLC.

Table 1. A compositional analysis of the glasses included in the study.

Sample	mol%				
	K ₂ O	Na ₂ O	SiO ₂	SnO	SnO ₂
1	14.0	—	53.1	32.6	0.3
2	—	12.6	55.7	31.0	0.7
3	—	25.8	53.2	18.1	2.9
5	—	—	47.0	53.0	—
	MgO	Na ₂ O	SiO ₂	CaO	SnO ₂
4	5.9	10.6	66.4	7.5	2.7
	Rb ₂ O	Li ₂ O	SiO ₂	SnO	SnO ₂
6	—	13.6	49.0	37.0	0.4
7	5.0	—	45.0	50.0	—

of $\text{Ca}^{119}\text{SnO}_3$ and spectra were taken in conventional transmission geometry using a double-ramp wave form which, when velocity increasing and decreasing ramps are combined, gives the spectrum on a flat background. An intrinsic germanium detector was able to resolve the 23.9 keV Mössbauer source ray from the adjacent 25.4 keV x-ray, which significantly improved the signal to noise ratio of the spectra.

Samples were run at 4.2 K in fields applied by a Helmholtz pair of superconducting coils. It was found that a geometry in which the applied field was perpendicular to the γ -ray direction was most sensitive in showing the effect of the sign of the quadrupole interaction. Spectra were taken in applied fields up to 9 T in magnitude.

Table 2. Values returned from the fitting program of the principal hyperfine parameters B , Δ , δ and Γ .

Sample	B (T)	Δ (mm s ⁻¹) δ (mm s ⁻¹) Γ (mm s ⁻¹)		
		All errors ± 5 in the 2nd decimal place		
1	0	1.92	2.61	1.01
	3	1.92	2.64	1.04
	6	1.98	2.63	1.15
	9	1.94	2.64	1.30
2	0	1.97	2.78	1.04
	9	2.09	2.81	1.30
3	0	1.95	2.68	0.98
	3	1.98	2.69	0.98
5	0	2.06	2.98	1.13
	9	2.13	2.97	1.39
6	0	2.01	2.87	1.16
	7	1.96	2.83	1.17
7	0	2.06	2.89	1.26
	6	2.06	2.87	1.22

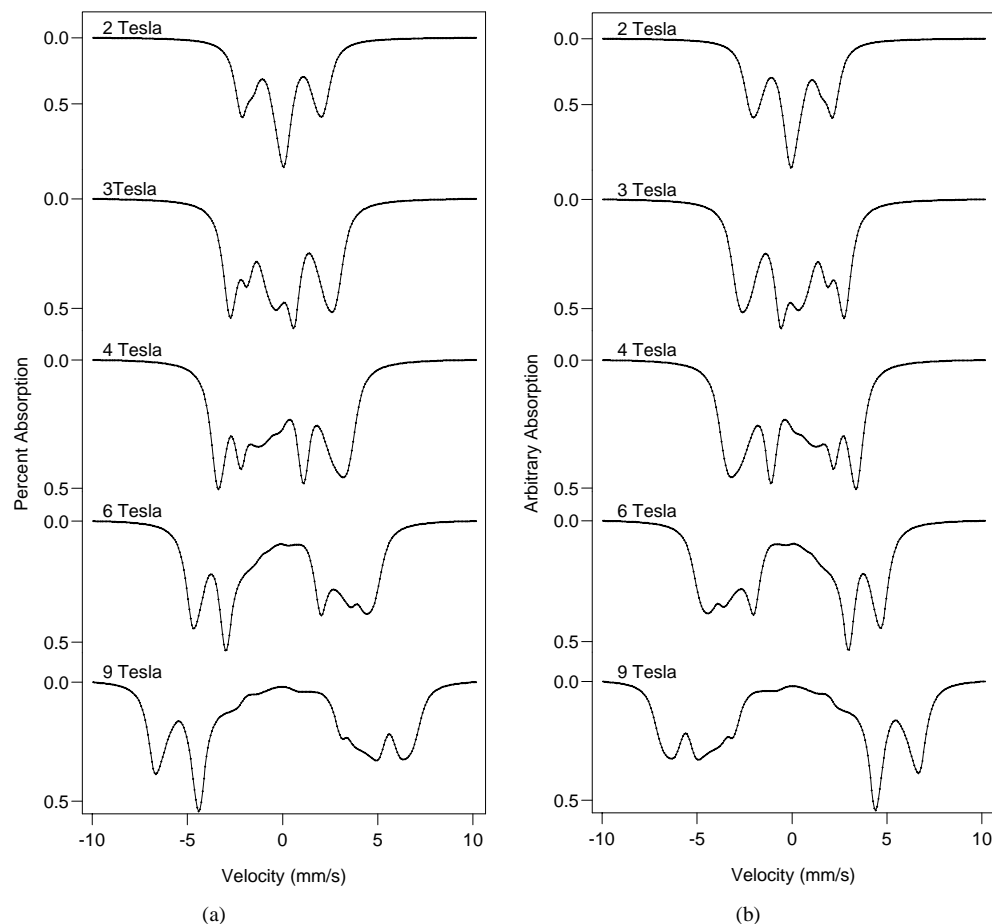


Figure 1. (a) A simulation of applied field spectra for $\delta = 0 \text{ mm s}^{-1}$, $\Gamma = 1 \text{ mm s}^{-1}$, $\Delta = 2 \text{ mm s}^{-1}$ and various values of B . (b) A simulation of applied field spectra for $\delta = 0 \text{ mm s}^{-1}$, $\Gamma = 1 \text{ mm s}^{-1}$, $\Delta = -2 \text{ mm s}^{-1}$ and various values of B .

2.3. The fitting program

The fitting program used the Hamiltonian matrix as described by Kundig [8]. The glass powders contain no internal field, and so the field in the Hamiltonian is the applied field. The glass was assumed to possess a completely random orientation of EFGs with respect to the applied field (true for both powdered and non-powdered samples). Thus a version of the fitting program that integrated over all possible orientations of \mathbf{B} with respect to the EFG was used. For each orientation the integration was accordingly weighted by $\sin \theta$ (where θ denotes the angle between the EFG principal axis and \mathbf{B}) with orientations of \mathbf{B} lying on the xy plane of the EFG axis (i.e. when $\theta = 90^\circ$) given maximum weighting. The contribution of each orientation was in the standard form of Lorentzian linewidth profiles and these were accumulated to generate the overall envelope of the complete spectrum. Steps of 5° in θ were considered to be adequate for generating accurate spectra.

Simulations of predicted spectra were generated by fixing a single value for quadrupole interaction (Δ), applied magnetic field (\mathbf{B}), and absorption linewidth (Γ). The EFG asymmetry (η) was set to be zero for reasons discussed in section 4. Typical simulations

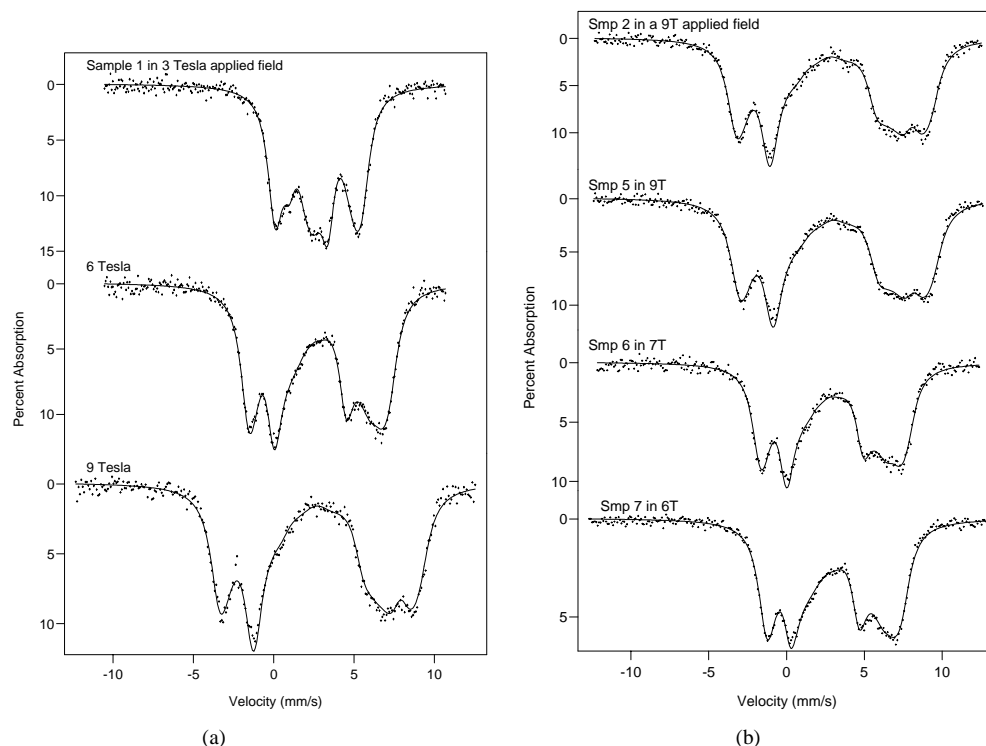


Figure 2. (a) Applied field spectra of the $\text{K}_2\text{O}:\text{SnO}:\text{SiO}_2$ (sample 1) glass at various values of B . (b) Applied field spectra of $\text{Na}_2\text{O}:\text{SnO}:\text{SiO}_2$ (sample 2), $\text{SnO}:\text{SiO}_2$ (sample 5), $\text{Li}_2\text{O}:\text{SnO}:\text{SiO}_2$ (sample 6) and $\text{Rb}_2\text{O}:\text{SnO}:\text{SiO}_2$ (sample 7) glasses at various values of B .

are shown in figure 1(a) and (b) where it is apparent that distinct asymmetrical spectra are generated for significant fields and quadrupole splitting. This illustrates the possibility of identifying the sign of e^2qQ . Two spectra sharing the same values for all parameters except the sign of e^2qQ are exact mirror images of each other (compare figure 1(a) to (b)). Further simulations revealed that for diminishing Δ the asymmetry becomes less distinct and that a field greater than 3 T is required to provide adequate resolution to expose such an asymmetry, irrespective of Δ value. It may also be noted that it is easier to ascertain the sign of e^2qQ when the direction of observation is perpendicular to the applied field.

3. Results

The coupling constant e^2qQ was determined to be positive for the Sn^{2+} valence state in all the cases examined and the spectra of the glasses, taken at a range of applied field values, are shown in figure 2. These spectra correlated well to the simulated spectra of figure 1 and it was possible to generate good fits by incorporating a least-squares minimization routine into the program. Values of χ^2 were consistently less than two with the four free parameters isomer shift (δ), Δ , B , and Γ . Although the applied field was of known magnitude, it was set as a free parameter in the fitting process. The consequent values agreed within error with the known field from the calibrated magnet. Fitted values for these parameters are listed in table 2.

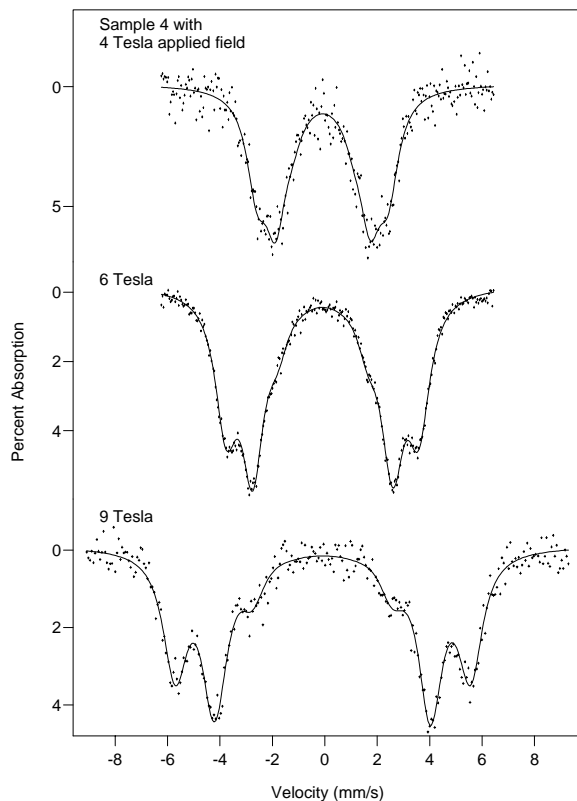


Figure 3. Applied field spectra of SnO_2 present in doped float glass (sample 4). The isotropic spectra are a direct result of a small quadrupole splitting.

Values for Γ of around $1.05 \pm 0.1 \text{ mm s}^{-1}$ for the Sn^{2+} component in all the glasses were consistent with broadening effects [9] caused by a 2D distribution in the magnitude of the principal hyperfine parameters δ and Δ . This is due to the range of environments experienced by the Sn^{2+} ion in the glass.

4. Discussion

The observation of a definitive sign for the EFG shows that the environment is similar at all the Sn^{2+} sites, i.e. that there is some structural short-range order. For an isolated Sn^{2+} ion the outer electron configuration is $5s^2$, which is spherically symmetric with zero EFG. Several possible bond structures and co-ordinations of the Sn atom to the surrounding O atoms could be responsible for the observed EFG at the nucleus [10]. The most probable involve Sn–O bonds of strong directional and covalent nature, with $s^a p^b d^c$ hybridization of the valence shell electron wavefunctions. The large magnitude and the determination of a positive $e^2 q Q$ indicates (for a negative Q) a dominant contribution to the net EFG by the non-bonding lone pair (which possesses strong p_z character) over that of the bonding hybrid orbitals. The EFG at any particular Sn site will most probably not possess axial symmetry, but it is not possible to determine it from the spectra.

Furthermore, with the random nature of the inevitable small variations in the contributions to the EFG from both the hybrid bond charge distribution and (in the case of the ternary glasses) the charge surrounding alkali metal cations, η is likely to have a distribution of values along with e^2qQ . However simulated spectra for realistic and non-zero η (with $e^2qQ = 2 \text{ mm s}^{-1}$) showed such a minimal effect on the spectra that they could not be resolved in experimental spectra without much improved counting statistics. Hence η was set to zero in the fitting process.

Sn^{4+} has a closed-shell electron configuration, and hence only a small quadrupole splitting (typically 0.4 mm s^{-1}). The fits of Sn^{4+} in sample 4 (doped float) are shown in figure 3. The applied field spectra are very symmetrical and, even with very good counting statistics, are very difficult to utilize in ascertaining sign. It is possible that Sn^{4+} sits in a variety of sites which could lead to equal positive and negative quadrupole interactions, and hence no net quadrupole splitting. This would make the high-field spectra totally symmetric. It would be interesting to obtain very well defined spectra by counting for much longer times in order to test whether there is short-range order at the Sn^{4+} sites.

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