1772 *Chem. Mater.* **1993,** *5,* 1772–1774

Solid-State NMR Studies of Two Phases for Tin Hexathiohypodiphosphate

David C. Apperley† and Robin K. Harris*,‡

Industrial Research Laboratories and Department of Chemistry, University of Durham,
South Road, Durham DH1 3LE, England

David A. Cleary

Department of Chemistry, Gonzaga University, Spokane, Washington 99258-0001

Received August 3, 1993. Revised Manuscript Received October 4, 1993®

Magic-angle spinning ^{31}P and ^{119}Sn NMR spectra of $Sn_2P_2S_6$ are presented. Spectra were recorded at room temperature, 80 °C, and 100 °C. Two distinct center-band resonances are observed both for the phosphorus and for the tin spectra at room temperature. When the temperature is raised above the ferroelectric phase-transition temperature ($T_c \sim 70$ °C), both phosphorus and tin show single center-band resonances. These results are generally consistent with earlier structural characterization. The spinning sideband patterns at both low and high temperatures were analyzed in order to determine the principal components of the shielding tensor. Consideration of the ^{31}P shielding tensor suggests that the point symmetry at the phosphorus site in the room-temperature phase is less than that implied by X-ray analysis.

Introduction

The post-transition-metal phosphorus chalcogenide $Sn_2P_2S_6$ has received considerable attention due to its ferroelectric behavior.[1] Recently, we demonstrated that $Sn_2P_2S_6$ also exhibits a significant nonlinear-optical response.[2] In our earlier structural work, the nature of the transition from the ferroelectric phase to paraelectric phase was characterized as second order based on differential scanning calorimetry measurements.[3] The details of the high-temperature phase of $Sn_2P_2S_6$ remained unclear. There is a residual nonlinear-optical response above the phase transition, which imposes certain symmetry requirements (namely a polar axis), yet structural characterization has a yielded a solution incompatible with these requirements.

One solution to this problem may lie in the dynamical behavior of the tin atoms. The phase transition can be viewed as the cooperative movement of tin atoms within a rigid P_2S_6 framework. The formal oxidation state of the tin atoms is +2, and therefore they can be expected to exhibit an "inert pair" effect similar to that observed in PbO.[4] This effect causes the metal atoms to be displaced from the center of a coordination sphere. To probe the dynamical behavior of the tin atoms in $Sn_2P_2S_6$, we have commenced a variable-temperature NMR study of the ^{31}P and ^{119}Sn nuclei. In this paper, we report our initial findings for the ferroelectric phase (room temperature) and paraelectric phase (80 and 100 °C) of $Sn_2P_2S_6$.

Table I. Magic-Angle Spinning NMR Data for $Sn_2P_2S_6$

nucleus	temp[a]/ °C	δ_{iso}/ ppm	$\lvert J_{SnP}\rvert$/ Hz	ν_r[h]/ Hz	ζ[e,i]/ ppm	η[i]	N[g]
phosphorus-31	ambient	93.71[c,d]	236[b,c]	1620	−27.0	0.67	9
		89.20[c,d]	229[b,c]	1620	−38.0	0.41	9
	100	92.12	*f*	1830	−30.7	0.50	8
tin-119	ambient	−754.5	*f*	9750	213	0.69	7
		−782.5	*f*	9750	329	0.18	9
		−760.4	*f*	11900	222	0.64	5
		−786.1	*f*	11900	323	0.15	5
	80	−783.4	*f*	8900	272	0.16	7
		−781.3	*f*	11700	276	0.21	7

[a] Nominal. [b] Equal within experimental error. [c] Obtained from a spectrum with $\nu_r = 4390$ Hz, using resolution enhancement. [d] $|J_{PP}| = 66$ Hz. [e] The sign uses the *shielding* convention (opposite to that for δ). [f] Not obtained (even from a spectrum with $\nu_r = 4140$ Hz). [g] Number of spinning sidebands (including the center band) fitted. [h] Spinning speed. [i] Shielding tensor parameters. For their definition, see the text.

Solid-State NMR Spectra

(i) Phosphorus-31 Region. At ambient probe temperature, the ^{31}P spectrum of $Sn_2P_2S_6$ under conditions of magic-angle spinning (4.4 kHz) consists of two center bands at $\delta_P = 93.71$ and 89.20 ppm (see Table I). Additional fine structure is visible, and resolution enhancement (Figure 1) reveals splittings which yield coupling constants $|J_{PP}| = 66$ Hz and $|J_{SnP}| = 171$ and 163 Hz, respectively. Since the line widths are substantial (~50 Hz) the (Sn,P) couplings can be regarded as equal within experimental error. Resolution is lost at both low and high spinning speeds. In the former case this arises because of homonuclear (P,P) dipolar coupling, and in the latter because of rotation-induced heating. In principle, homonuclear J coupling can produce a variety of splitting patterns under MAS conditions,[5] but in the present case the spectra are interpretable on a simple first-order basis. The NMR observations, in agreement with the diffraction results,[6,7]

---

† Industrial Research Laboratories.

* Department of Chemistry.

‡ To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) Carpentier, C. D.; Nitsche, R. *Mater. Res. Bull.* **1974,** *9,* 1097.

(2) Cleary, D. A.; Willett, R. D.; Ghebremichael, F.; Kuzyk, M. G. *Solid State Commun.* **1993,** *88,* 39.

(3) Scott, B.; Pressprich, M.; Willett, R. D.; Cleary, D. A. *J. Solid State Chem.* **1992,** *96,* 294.

(4) West, A. R. *Solid State Chemistry and Its Applications*; Wiley: Chichester, 1984; p 314.

(5) Kubo, A.; McDowell, C. A. *J. Chem. Phys.* **1990,** *92,* 7156. Challoner, R.; Nakai, T.; McDowell, C. A. *J. Chem. Phys.* **1991,** *94,* 7038.

(6) Dittmar, G.; Schäfer, H. *Z. Naturforsch. B* **1974,** *29,* 312.

0897-4756/93/2805-1772$04.00/0

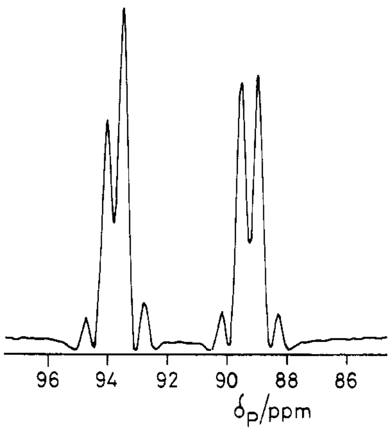

Figure 1. Phosphorus-31 MAS NMR spectrum of $Sn_2P_2S_6$ at 121.42 MHz and ambient probe temperature, center bands only, with resolution enhancement to reveal (P,P) and (Sn,P) coupling. The satellite peaks arise from the coupling to Sn (principally ^{119}Sn), but half these lines are obscured under the major resonances. Spectrometer operating conditions: pulse angle 90°; relaxation delay 60 s, number of transients 8; spinning rate 4390 Hz.

indicate that the asymmetric unit contains a complete P_2S_6 group, the two ^{31}P nuclei being nonequivalent. Spinning sideband analysis shows (Table I) that the shielding anisotropy is modest and the asymmetry relatively high for both phosphorus nuclei, with significant differences between the two sites. The large asymmetries reveal that the statement by Dittmar and Schäfer[6] of "nearly undistorted point group symmetry $3m$" is somewhat misleading.

At 100 °C (nominal), the ^{31}P spectrum is simplified, showing there is only one site for phosphorus, in agreement with the crystal structure of the high-temperature form.[7] Coupling information is no longer available. The isotropic chemical shifts and all the shielding tensor parameters (Table I) lie between the corresponding results for the two nonequivalent ^{31}P nuclei of the room-temperature form. As far as the P_2S_6 unit is concerned, the phase change simply results in the achievement of a more equivalent (averaged) environment for the two PS_3 moieties.

(ii) Tin-119 Region. The ^{119}Sn MAS NMR spectrum of $Sn_2P_2S_6$ at ambient probe temperature is shown in Figure 2a. As expected from the crystal structure,[6,7] there are two center bands, each with its own spinning sideband manifold. The data, including the results of spinning sideband analysis, are given in Table I. The difference in isotropic shift between the sites (ca. 27 ppm) is modest and does not indicate a significant difference in coordination. The description of the tin environment as being effectively 8-fold coordination in both cases is therefore preferred to the differentiation of 7- and 8-fold arrangements. However, both the shielding anisotropies and the asymmetry parameters are substantially different between the sites. The anisotropies are relatively modest for ^{119}Sn, which is not surprising since all the coordinating atoms are of the same element. However, one site has a significantly higher asymmetry. It is tempting to assign this as the site said to be 7-coordinate by Dittmar and Schäfer,[6] but this is speculative. Our experiments do not, of course, reveal the orientation of the principal axis system in the molecular frame.

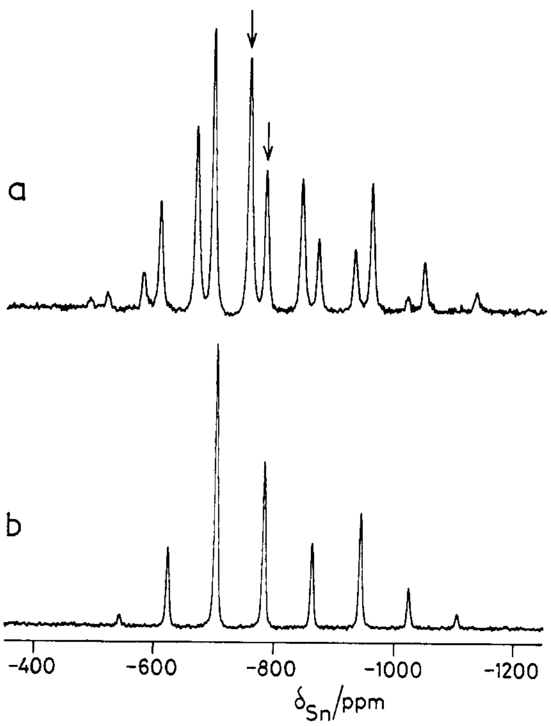

Figure 2. Tin-119 MAS NMR spectra of $Sn_2P_2S_6$ at 111.86 MHz: (a) at ambient probe temperature; (b) at 80 °C (nominal). The center bands are indicated by arrows. The spectrometer operating conditions were pulse angle 90°, relaxation delay 1 s, number of transients 1000 (a) and 500 (b), and spinning rate 9750 Hz (a) and 8900 Hz(b).

The high-temperature phase gives a spectrum (Figure 2b) with only one center band, as expected. The full data for this phase are given in Table I. The isotropic chemical shift is close to that of the lower-frequency site of the low-temperature phase, as is the shielding asymmetry, though the anisotropy is midway between the values between the two low-temperature sites. Overall, these data are consistent with the X-ray results[3] which show that the environment in the high-temperature phase is more clearly 8-fold coordinate (the Sn···S distances covering only the range from 2.914 to 3.227 Å) than for the sites in the low-temperature phase.

The ^{119}Sn NMR chemical shifts for the low-temperature phase show a pronounced dependence on the spinning speed, as is exemplified in Table I. The values range from −750.6/−779.5 ppm at 7.2 kHz to −760.4/−786.1 ppm at 11.9 kHz. We attribute this to a temperature dependence caused by spinning.[7] Our measurements suggest that the temperature range in the above experiments is from ~35 °C at 7 kHz to ~60 °C at 12 kHz. It is expected that there may be a temperature gradient within the sample contributing to the ^{119}Sn line widths, which are typically ca. 1 kHz for the low-temperature phase and a little smaller for the high-temperature phase (but in both cases obscuring any splitting due to Sn,P coupling).

Experimental Section

Synthesis. Large single crystals of $Sn_2P_2S_6$ were prepared from the constituent elements at high temperature. Stoichiometric amounts of tin, phosphorus, and sulfur (plus some iodine which serves as a transporting agent) were ground together and then transferred to a quartz reaction tube. The sample was evacuated, sealed, and placed in a horizontal tube furnace. Crystal growth occurred over a temperature gradient of 630–600 °C/20 cm. Large (1 × 1 × 1 cm) massive crystals of $Sn_2P_2S_6$ were

---

(7) Bjorholm, T.; Jakobsen, H. J. *J. Magn. Reson.* **1989**, *84*, 204.

realized after a few days. These crystals were ground to a powder (orange) for the NMR experiments. As the product appears to be air stable, no special handling precautions were taken.

Spectroscopy. Spectra were recorded using a Varian VXR 300 spectrometer operating at 121.42 and 111.86 MHz for ^{31}P and ^{119}Sn, respectively. A Doty Scientific fast-spinning MAS probe was employed, with 5-mm-o.d. silicon nitride rotors and end-caps made of Vespel. Temperature variation was achieved by heating the bearing air, the temperatures being sensed by a thermocouple in the air supply line. The temperatures quoted are nominal (based on input air at 21 °C), and are used solely to relate to the phase of $Sn_2P_2S_6$ required. Chemical shifts were referenced, using the high-frequency-positive convention, with respect to the signals for 85% H_3PO_4 and Me_4Sn, for ^{31}P and ^{119}Sn, respectively, by replacement. The spinning sidebands were analyzed iteratively to obtain shielding tensor information using a computer program developed in-house,[8] based on the equations of Maricq and Waugh.[9] Shielding tensor data are reported with the opposite sign convention to the chemical shifts, using as definitions: anisotropy, $\zeta = \sigma_{33} - \sigma_{iso}$, and asymmetry $\eta = (\sigma_{22} - \sigma_{11})/\zeta$, with components defined by $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$.

Conclusions

Phosphorus-31 and tin-119 NMR data for the ferroelectric and paraelectric phases of $Sn_2P_2S_6$ are reported. The results are consistent with earlier structural work which concluded that at room temperature the structure consists of two distinct tin atoms in the asymmetric unit, rendering the two phosphorus nonequivalent as well. Above the phase transition the tins become equivalent as do the phosphorus nuclei, and this is borne out by the NMR findings. Analysis of the spinning sideband patterns yields the principal components of the shielding tensors. These values are not entirely consistent with earlier structural work and suggest that the point symmetry for the phosphorus sites at room temperature is significantly less than $3m$. It is clear from this work the MAS NMR is a useful tool in the study of temperature-dependent effects in $Sn_2P_2S_6$. For further insight into behavior of this system, detailed T_1 measurements will be required.

Acknowledgment. We thank the U.K. Science and Engineering Research Council for access to the National Solid-State NMR Service based at Durham.

---

(8) Ascenso, J. R.; Bai, H.; Merwin, L. H.; Harris, R. K., details unpublished.

(9) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300.