Intermolecular Bonding and Characteristic Lattice Temperatures in Organotin Halides

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Summary A set of Debye temperatures and characteristic temperatures of organotin halides is given based on Mössbauer spectroscopic measurements and Thirring's expansion of frequency moments, confirming that the second negative moment is directly related to the mean-square vibrational amplitude in the Debye–Waller factor and that the extent and types of intermolecular forces in strongly co-ordinated polymers are quite different from those in monomers.

IT was recently shown that the extent of intermolecular bonding in organotin molecular solids can strongly influence the mean-square vibrational amplitude, $<u^2>$, of the tin atom[1] and can lead to changes of optical vibrational frequencies of the various tin–ligand groups.[2] Mössbauer effect,[3] *X*-ray,[4] and neutron scattering[5] crystallographic studies have confirmed the polymeric structures of R_3SnF, R_2SnF_2, and R_2SnCl_2, R = Me or Ph. We have measured the lattice dynamic parameters in the range 70—298 °K and found an important relation between the degree of intermolecular interaction and the lattice characteristic temperature in organotin halides.

TABLE. *Characteristic lattice temperatures for organotin halides*

Compound	Frequency moment $\bar{\nu}$ (−2) cm^{-1}			Characteristic temperatures, θ_∞ °K			Debye temperatures θ_D °K		
	70° K	170° K	190° K	70° K	170° K	190° K	70° K	170° K	190° K
β-Sn metal	55·7	53·11	53·1	138·3	131·9	131·9	131·4	134·3	133·8
Ph_4Sn	45·1	42·2	43·5	112·2	104·9	108·1	113·5	105·2	105·0
Ph_3SnF	49·7	43·4	45·2	112·6	108·2	112·2	113·6	107·0	107·2
Ph_3SnCl	36·7	—	—	91·1	—	—	87·65	88·7	—
Ph_2SnCl_2	40·5	39·5	38·3	100·6	98·1	95·0	100·7	98·1	97·3
$PhSnCl_3$	36·4	36·9	—	90·4	91·7	—	88·4	89·9	90·4
Me_4Sn	30·26	31·30	—	75·2	77·7	—	71·0	77·0	—
Me_3SnF	42·2	42·7	44·8	104·8	106·0	111·3	102·8	102·3	103·5
Me_3SnCl	36·82	—	—	91·5	—	—	90·7	—	—
Me_2SnCl_2	43·8	44·5	39·3	108·9	110·6	97·6	108·3	111·0	110·8
Me_3SnBr	31·44	—	—	78·14	—	—	65·8	—	—
Me_2SnBr_2	43·6	43·9	—	108·5	109·0	—	105·0	103·0	105·0

In the Debye approximation, the recoilless fraction, f_a, in Mössbauer resonance absorption is $f_a = \exp(-2W)$, where $2W$ is the Debye–Waller factor and is given by

$$2W = \frac{3E_\gamma^2 T}{Mc^2 k_B \theta_D^2} \text{ for } T > \theta_D/2$$

T and θ_D are absolute and Debye characteristic temperatures in °K respectively. Letting M equal the mass of the tin atom, we have calculated θ_D at various temperatures (Table). Alternatively, we have evaluated the characteristic lattice temperatures in the quasiharmonic approximation from the frequency moment method[6] in terms of the mean-squared vibrational amplitude,

$$\langle u^2 \rangle = \frac{k_B T}{M}\left[\frac{1}{\omega^2(-2)} + \frac{1}{12}\left(\frac{\hbar}{k_B T}\right)^2 - \frac{1}{720}\left(\frac{\hbar}{k_B T}\right)^4 \omega^2(2)\right]$$

where $\omega(n)$ are the moments of the frequency distribution. For molecular crystals a characteristic lattice temperature is approximated by[7]

$$\theta_\infty = \hbar/k_B \sqrt{3}\,\omega(-2)$$

$\omega(-2)$, reported in terms of wave numbers $[\bar{\nu} = \omega(-2)/2\pi c]$, and θ_∞ for the organotin halides are listed in the Table. The choice of M is necessarily ambiguous in view of the complexities associated with molecular dynamics.

An analysis of θ_D and θ_∞ shows that the lattice characteristic temperatures are significantly larger for the polymeric structures compared to the monomeric type, especially at higher temperatures. For example, θ_D or θ_∞ is 25% larger for the polymeric Me_3SnF compared to the monomeric Me_4Sn. Although these differences follow in a natural way from theoretical considerations, there is probably no sharp distinction in the lattice dynamic behaviour of solid molecular polymers and monomers. Instead, the extent and types of intermolecular forces in these solids are sufficiently diverse to allow for a gradual change in lattice potentials as one goes from a monomer to a strongly co-ordinated polymer net.

In the case of Me_2SnCl_2 we observed a spatial anisotropy in $<u^2>$ due to the lattice dynamic nature of polymeric layer structures. The temperature dependence of the line intensities is $I_2/I_1 = 1{\cdot}0707 + 7{\cdot}9749 \times 10^{-4}T$ between 70 and 210° K, where I_2 corresponds to the line of higher γ-ray energy with respect to a moving emitter; the major component of the electric field gradient tensor $V_{zz} < 0$.

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