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Mössbauer lattice temperature of tetragonal ($P4/nmm$) SnO

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The lattice-dynamical properties of tetragonal (black) SnO (with space-group symmetry $P4/nmm$) have been examined over the temperature range $78 \leq T \leq 300$ K by variable-temperature ^{119}Sn Mössbauer-effect measurements. The lattice temperature calculated from the temperature dependence of the recoil-free fraction (assuming the atomic mass) is 229 K. Using the effective vibrating mass calculated from the temperature dependence of the isomer shift ($M_{\text{eff}} = 169$ g mol^{-1}) leads to a lattice temperature of 193 K. The quadrupole-coupling hyperfine parameter is only weakly temperature dependent over the above temperature range, and there is no evidence of a vibrational anisotropy parallel and perpendicular to the fourfold rotational axis through the metal atom. The recoil-free fraction at 295 K is 0.35 ± 0.02.

INTRODUCTION

In connection with a recent study[1] of the ion-implantation—caused radiation damage in thin films of β-Sn and single-crystal SnS_2, it became necessary to make use of the ^{119}Sn Mössbauer parameters of tetragonal (black) SnO, and in particular the lattice temperature as probed by the Debye-Waller factor. Although the isomer shift (IS) and quadrupole splitting (QS) parameters of Sn(II) oxide have been reported by a number of authors,[2,3] there appears to have been only a single study reported[4] of the temperature dependence of the recoil-free fraction over the range $100 \leq T \leq 480$ K. Since the main focus of that study was in the characterization of amorphous Sn(IV), no special emphasis was placed on the characterization of the SnO used in these measurements. Moreover, the description of this material as "gray" leaves open the question of whether the sample used was free of contamination from other divalent tin oxides or hydroxides. Such species are expected to have very similar hyperfine parameters[3] as SnO, and thus may not have been detected (especially at relatively low concentrations) in the Mössbauer spectra. In this context it should be noted that a red metastable form[5] of SnO has a significantly different structure [with space-group-symmetry $Pbcn$ (D_{2h}^{14})] with eight formula units per unit cell. Not unexpectedly, this form has significantly different ^{119}Sn Mössbauer parameters at 80 K, and its presence in the subject compound can be ruled out on the basis of linewidth considerations, as will be discussed below. Finally, it is noted that the presence or absence of a Goldanskii-Karyagin effect in the black form of SnO has not yet been established. The present study on a well-characterized sample of SnO was undertaken to determine the relevant parameters of this material in the temperature range $78 \leq T \leq 300$ K, particularly as these relate to the lattice-dynamical properties of the metal atom in this compound.

EXPERIMENTAL

Black SnO was obtained from Fisher Scientific Co. (American Chemical Society Certified Reagent) and washed several times with distilled water and subsequently dried in a vacuum dessicator over MgO. A sample of this material was examined with respect to its powder x-ray pattern with Cu $K\alpha$ radiation, using a Phillips Model PW1050 diffractometer periodically calibrated with elemental Si. All nine diffraction peaks lying in the interval $29.87° \leq 2\theta \leq 62.53°$ were matched within 2% of the line positions reported in the literature.[6,7] In addition, there is a medium strong diffraction peak at $2\theta = 80.3°$ not previously reported. ^{119}Sn Mössbauer experiments were carried out on thin samples of the subject material (either as neat powder layers sandwiched between Al foil or as a pellet compressed at 20 000 psi with BN or an inert carbohydrate as a dispersant) using the spectrometer and temperature controller described earlier.[8] Spectrometer calibration at 296 ± 2 K was affected using metallic iron as a reference absorber. All isomer shifts are reported with respect to a spectrum of $BaSnO_3$ at room temperature. Data reduction was effected using the MINCON program modified to run on a Digital Equipment Corp. PDP11/34 computer (with 64 kilobytes of core memory),[9] or the SPECTRA program modified to run on an IBM 370/158 computer.[8]

RESULTS AND DISCUSSION

The relevant parameters extracted from the temperature-dependent ^{119}Sn Mössbauer experiments are summarized in Table I. The room-temperature values for the IS and QS parameters (2.64 and 1.31 mm sec^{-1}, respectively) are in reasonably good agreement with the results reported by Collins *et al.*[5] A number of other values of these parameters, both at room temperature and liquid-nitrogen temperature has been reported,[2,3,10] but in a number of instances the calibration of the isomer shift scale is somewhat uncertain. A typical spectrum is shown in Fig. 1.

The observed linewidths of the ^{119}Sn resonance lines in the interval $180 \leq T \leq 300$ K where the thin absorber approximation is most justified (*vide infra*) are temperature independent, and have a mean value of 0.853 ± 0.016 mm sec^{-1}. This value is significantly broader than twice the natural linewidth based on lifetime measurements, but is narrower than the values previously reported.[4] The small extraneous broadening which is observed is assumed to be due primarily to source effects and will not be considered further in the subsequent discussion. The observed linewidths indicate that there is a single unique tin site in the SnO samples examined, in consonance with the x-ray powder diffraction results cited above, and that impurity effects, if any, are present below the ^{119}Sn Mössbauer detection limit. The presence of the red form[5] of Sn$^{\mathrm{II}}$O can be ruled out on the basis of its large QS (2.20 mm sec^{-1} at 80 K), which would have been readily detected in the ^{119}Sn spectra.

The temperature dependence of the isomer shift for SnO in the temperature range $78 \leq T \leq 300$ K is moderately well fitted by a linear relationship. A typical data set is summarized graphically in Fig. 2. The correlation coefficient to the linear regression indicated by the solid line is 0.966 for the ten data points. From this temperature dependence it is possible to calculate an effective vibrating mass M_{eff} using the relationship[11]

$$\frac{d\delta_{\mathrm{IS}}}{dT} = -\frac{3}{2}\frac{E_\gamma k_B}{M_{\mathrm{eff}}c^2} \, . \tag{1}$$

From the observed temperature dependence of δ_{IS} (Table I) the value of M_{eff} calculated for SnO is 168 ± 18 g mol^{-1}. The considerable ($\pm 11\%$) uncertainty in this value arises from the relatively small variation of δ_{IS} with temperature (compared with the natural linewidth) in ^{119}Sn Mössbauer spectra. Nonetheless, it is clear that this value is significantly larger than the formula weight and reflects the covalency of the tin—oxygen bonding interaction. The percent covalency ($\sim 63\%$) in the Sn—O bond has been estimated[10] from the Hannay-Smyth equation.

The quadrupole-splitting hyperfine parameter for SnO over the above temperature range is also weakly temperature dependent, having a slope of $\sim 0.75 \times 10^{-4}$ mm sec^{-1} K^{-1}. This effect primarily reflects the thermal expansion of the SnO lattice between liquid-nitrogen temperature and room temperature. There is no evidence from these data of a crystallographic phase change between the two temperature extremes.[12]

As has been noted previously,[13] for a thin absorber the temperature dependence of the recoil-free fraction for the 23.8-keV γ-ray transition in ^{119}Sn is well represented by the temperature dependence of the area under the resonance curve. A representative data set (in which the areas are normalized to the 78-K data point to facilitate intersample comparison) is summarized graphically in Fig. 3. The correlation coefficient for the linear regression indicated by the solid line is 0.996 for the ten data points. From this temperature dependence it is possible to extract a lattice temperature as probed by the ^{119}Sn Mössbauer active atom, using the relationship valid in the high-temperature limit,

$$\frac{d\ln A}{dT} = -\frac{6E_R}{k_B\Theta_M^2} \, , \tag{2}$$

TABLE I. Summary of ^{119}Sn Mössbauer data for tetragonal SnO.

	78 K		300 K
δ_{IS} (mm sec^{-1})$^{\mathrm{a}}$	2.697 ± 0.018		2.641 ± 0.019
Δ_{QS} (mm sec^{-1})	1.332 ± 0.017		1.308 ± 0.012
f	0.74 ± 0.03		0.35 ± 0.02
$d\ln[A(T)/A(78\ \mathrm{K})]/dT$ (K^{-1})		3.405×10^{-3}	
$d\delta_{\mathrm{IS}}/dT$ (mm sec^{-1} K^{-1})		2.465×10^{-4}	
M_{eff} [Eq. (1)] (amu)		168 ± 18	
Θ_M (K)		229 ± 3	
Θ'_M (K)		193 ± 2	
Mean Γ_{exp} ($180 \leq T \leq 300$ K) (mm sec^{-1})		0.853 ± 0.016	

[a] With respect to BaSnO$_3$ at 296 ± 2 K.

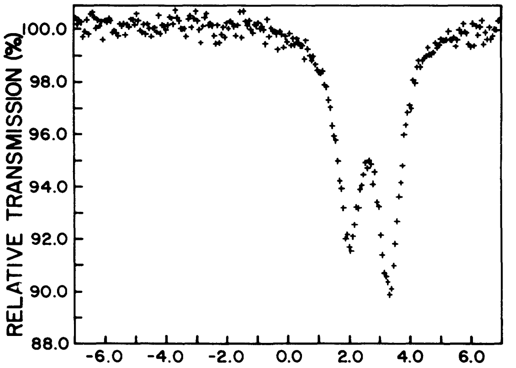

FIG. 1. Mössbauer spectrum of tetragonal SnO at 78 K. The isomer shift reference point is the center of a room-temperature spectrum of $BaSnO_3$, using the same Mössbauer source.

in which E_R is the recoil energy on γ-ray absorption in the absorber and Θ_M is the Debye-Waller temperature of the solid. On substitution for the recoil energy in terms of the Mössbauer γ-ray energy, Eq. (2) becomes

$$\frac{d\ln A}{dT} = -\frac{3E_\gamma^2}{k_B M_{\text{eff}} c^2 \Theta_M^2}\,, \tag{3}$$

which can be solved for Θ_M, provided M_{eff} is known. Using the atomic mass of ^{119}Sn leads to $\Theta_M = 229$ K. This value is somewhat higher than that reported by Collins *et al.* for their crystalline sample, and suggests that the effect of amorphous disorder in their samples may be even larger than previously discussed.[4] Substitution of $M_{\text{eff}} = 168$ amu, extracted from the second-order Doppler shift data [Eq. (1)] into (3), yields $\Theta_M' = 193$ K. This value cannot be compared to that for amorphous SnO since $\delta_{\text{IS}}(T)$ for such materials have not yet been reported.

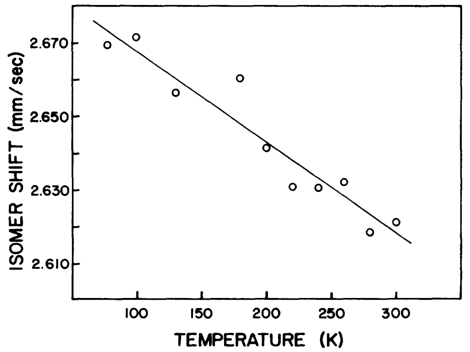

FIG. 2. Temperature dependence of the isomer shift of SnO. The solid line is a linear regression fit to the data with a correlation coefficient of 0.955 for the ten data points.

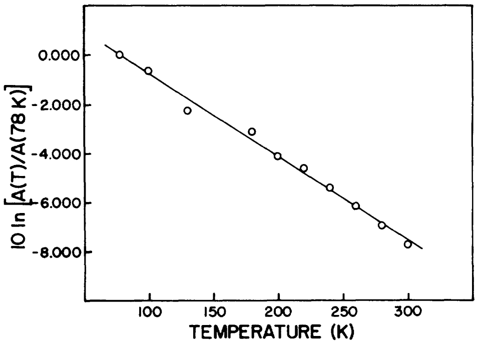

FIG. 3. Temperature dependence of the (normalized) area under the resonance curve for a sample of SnO dispersed in a carbohydrate matrix. The solid line is a linear regression fit to the data with a correlation coefficient of 0.996 for the ten data points.

For a thin absorber in the temperature regime where the high-temperature limiting equation (3) is valid, there is a one-to-one correspondence between f and Θ, namely

$$f = \exp\frac{-3E_\gamma^2 T}{k_B M c^2 \Theta^2}\,. \tag{4}$$

For ^{119}Sn at $T = 295$ K and using the atomic mass for tin leads to a relationship of the form

$$f = \exp\frac{-5.284\times 10^4}{\Theta^2}\,, \tag{5}$$

so that $\Theta = 229$ K implies f(SnO, 295 K) $= 0.37 \pm 0.02$.

As noted above, the temperature dependence of the isomer shift (second-order Doppler shift) can be used to estimate M_{eff}, and replacement of the atomic Sn mass in (3) then leads to $\Theta_M' = 193$ K. Use of the appropriate form of (5),

$$f = \exp\frac{-6.2283\times 10^6}{M(\Theta_M')^2}\,, \tag{6}$$

leads to f(SnO, 295) $= 0.37 \pm 0.02$, as expected.

Using the assumption that the temperature dependence of the recoil-free fraction scales linearly with the temperature dependence of the area under the resonance curve (thin absorber approximation) leads to f(SnO, 78) $= 0.74 \pm 0.03$. A value of f(SnO, 80) $= 0.55 \pm 0.03$ has previously been reported by Boltaks *et al.*[10]

Since the local environment around the metal atom in SnO is that of a square pyramid,[14,15] with the lone pair occupying the fifth vertex, it seemed plausible that there may be a significant vibrational anisotropy in the Sn motion parallel and perpendicular to the fourfold symmetry axis, especially in view of the layer structure of the solid. To estimate the magnitude of this effect, the temperature dependence of the area ratio of the two components of the doublet Mössbauer spectrum was examined in detail. Because of the platelike crystallographic morphology of black SnO, it is difficult to obtain a sample in which the crystals are randomly oriented with respect to the optical (γ-ray) axis, even when an inert material is used as an innocuous dispersant. Thus, even for the pelleted samples, the low-temperature (78-K) spectra showed a significant departure of the ratio R (defined as the ratio of the area at positive velocity with respect to the spectrum centroid to the area at negative velocity) from unity. The mean value observed at liquid-nitrogen temperature was 1.15 ± 0.02, and is presumed to be due principally to crystal orientation effects. To examine the temperature dependence (if any) of R in the range $78 \leq T \leq 250$ K, it is appropriate to subtract the low-temperature value from that observed at high temperatures, and the resultant variation of $R(T) - R(78\text{ K})$ with temperature is summarized in Fig. 4. The solid line represents a second-order polynominal regression, with the coefficients of the T and T^2 terms being $(7.6 \pm 3.2) \times 10^{-3}$ and $-(1.6 \pm 0.8) \times 10^{-6}$, respectively. It is immediately clear from these results that the temperature dependence of R is not dominated by a temperature-dependent vibrational anisotropy (Goldanskii-Karyagin effect), but rather by other factors which may contribute to small variations of R with temperature (including changes in the x-ray to γ-ray ratio as well as purely instrumental effects). This conclusion is based on the observations that the coefficient of the T^2 term is negative and that the curve in the low-temperature limit does not approach the abscissa asymptotically, both of which are required by the theory of the temperature-dependent recoil-free fraction anisotropy in molecular solids. Thus these data indicate that there is no appreciable vibrational anisotropy in the tin-atom motion parallel and perpendicular to the fourfold symmetry axis in SnO, in agreement with the observation of Pannetier and Denes[15] who have noted that the anisotropy of the thermal expansion of stannous oxide is smaller than normally noted in layer compounds having the PbO structure.

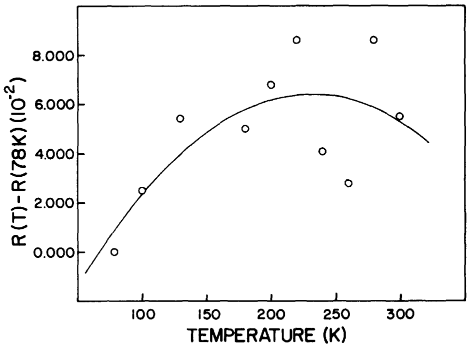

FIG. 4. Temperature dependence of the intensity ratio of the doublet Mössbauer spectrum of SnO. The quantity plotted (ordinate) is the observed value minus the value observed at $T = 78$ K and reflects effects other than those of crystal orientation, which is assumed to be temperature independent.

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