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Lattice Temperature and Hyperfine Interactions of $Pb_{1-x}Sn_xTe$ ($0.21 \leq x \leq 0.75$)

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Thin (<15 μm) samples of lead tin telluride, $Pb_{1-x}Sn_xTe$ (x = 0.21, 0.25, 0.55, and 0.75) have been studied by temperature dependent Mössbauer spectroscopy using the 23.8 keV gamma radiation of ^{119m}Sn. The tin atom occupies a lattice site having cubic symmetry (QS = 0 ± 0.020 mm sec^{-1}) over the temperature range $78 \leq T \leq 240$ K, and there is no evidence for a rhombic (low temperature) to cubic (high temperature) phase transition such as that reported for SnTe in this temperature interval. The lattice temperature as probed by the Sn atom is independent of the compositional parameter x and is similar to that reported for SnTe from Mössbauer studies and for $Pb_{0.63}Sn_{0.37}Te$ from X-ray powder diffraction data. Radiation damage produced by 2-MeV proton irradiation to a total fluence of $\sim 10^{17}$ cm^{-2} at liquid nitrogen temperature does not have any effect on the Mössbauer parameters, possibly because the major damage is annealed at temperatures below 150 K.

Introduction

Because of their potential use as infrared detectors, narrow band gap compound semiconductors have been the subject of extensive study and analysis over the past few years. This is especially true of the lead tin telluride (LTT) system and its two binary constituents, PbTe and SnTe, which have been well characterized (*1–3*) by a large number of physical techniques designed to elucidate the relationships between stoichiometry and electrical or optical characteristics. For solid state materials in which tin is a constituent, ^{119m}Sn Mössbauer effect spectroscopy has proven itself to be a fruitful—and frequently unique—technique for the examination of the lattice dynamical properties of the matrix and for the characterization of the electronic environment around the probe atom.

Lattice dynamical studies of SnTe, using both the 23.8 keV transition in ^{119m}Sn and the 35.5 keV transition in ^{125m}Te have been reported by Bukshpan (*4*) and by Keune (*5*). These authors were able to show that in the range $85 \leq T \leq 250$ K the characteristic lattice temperature calculated from the application of the Debye model to the temperature dependence of the recoil-free fraction is essentially the same for the two constituent atoms ($\theta_M(Sn) = 132 \pm 3$, $\theta_M(Te) = 141 \pm 5$ K). Bryukhanov *et al.* (*6*) have reported a similar value ($\theta_M(Sn) = 139 \pm 3$ K

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at 290 K), in contrast to the high temperature ($78 \leq T \leq 300$ K) data of Fano *et al.* (*7*) (θ_M(Sn) = 163.6 ± 5.0). These latter data, which have been analyzed in terms of a small temperature dependent quadrupole hyperfine interaction below ~160 K, are consistent with the X-ray data of Bocchi and Ghezzi (*8*) (who used the same samples as those studied by Fano *et al.*), but these authors concluded from their data that the Debye temperature of a sample of intermediate composition ($Pb_{0.63}Sn_{0.37}Te$) was 118 ± 4 K, with an average rms vibrational amplitude close to that of PbTe, and significantly different from that of SnTe.

Finally, in this context, it is worth noting that Bocchi and Ghezzi (*8*) observe that the lattice parameters between PbTe and SnTe change by only 2% and a recent study by Sternberg *et al.* (*9*) confirms that over this compositional range the dependence of the lattice parameter a for $Pb_{1-x}Sn_xTe$ is well described by $a = 6.42 - 0.10\,(x)$ Å. These results suggest that the mean square amplitudes of vibration (averaged over all atoms), and the lattice temperature as deduced from X-ray diffraction data for SnTe may be anomalous, and that these parameters ought to vary systematically with composition for these materials.

The present study on the system $Pb_{1-x}Sn_xTe$ was undertaken to attempt to clarify the relationship between the lattice dynamical properties and composition over a relatively large range of the lead to tin ratio, and to afford a comparison with related $Ge_{1-x}Sn_xTe$ solids recently reported by Fano *et al.* (*10*).

Experimental

Using the hot-wall technique (*11, 12*), thin samples of LTT were prepared on aluminum foil substrates at ~500°C. These samples were assumed to be identical to those reported by Weiser *et al.* (*12*), and were not further characterized with respect to elemental composition prior to study. Sample thickness was determined by direct weighting methods and showed that the $Pb_{1-x}Sn_xTe$ deposits were in the range of 2.6 to 6.5 mg cm^{-2}. Using a mean density of ~7.3 g cm^{-3} yields a lineal thickness range of 3.6 to 9 μm. Since the lattice temperatures of these samples, as probed by ^{119}Sn Mössbauer spectroscopy, *vide infra*, are ~140 K, the recoil-free fraction in these samples is ~0.06 at 295 K and ~0.5 at 78 K. These data, comparable to those for SnTe (*5, 6, 13, 14*), lead to a calculated value of the Mössbauer thickness t (defined by $t = n\sigma_0 f$, where n is the number of ^{119}Sn nuclei per cm^2, σ_0 is the cross section for recoiless scattering, and f is the recoil-free fraction) of ~0.02 to 0.3 (depending on x), and hence the "thin absorber approximation" is assumed to be valid in the subsequent data analysis. A $Ca^{119m}SnO_3$ source (*14*) at room temperature (295 ± 2 K) was used in conjunction with the constant acceleration spectrometer system described earlier (*15*). Data reduction was effected on the Rutgers University IBM 370/168 using a matrix inversion least squares procedure (*15*). Temperature control to ± 1 K or better over the time period necessary for data accumulation (typically 4 to 10 hr per spectrum) was achieved using a commercial (*16*) cryostat in conjunction with an NBS calibrated Au(0.07% Fe)-Chromel thermocouple. Spectrometer calibration was effected (*15*) using the magnetic hyperfine splitting in α-Fe at 295 K. All isomer shifts are reported with respect to the centroid of a standard $BaSnO_3$ absorber spectrum at 295 K.

Proton irradiations were carried out using the Rutgers 2 MeV van de Graaff on samples mounted at 45° to the beam axis and in thermal contact with an electrically insulated liquid nitrogen cooled cold finger which was part of a Faraday cup. Implantation dosage was calculated from the Faraday cup charge measurement. Typical damage runs consisted of $\sim 10^{17}$ protons/cm^2

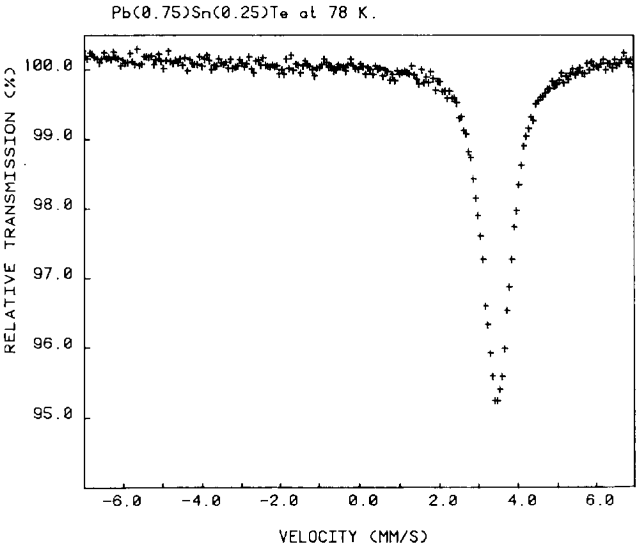

FIG. 1. ^{119}Sn Mössbauer spectrum of $Pb_{0.75}Sn_{0.25}Te$ at liquid nitrogen temperature. The isomer shift with respect to SnO_2 is 3.476 mm sec^{-1} and the full width at half maximum is 0.854 mm sec^{-1}.

and lasted several hours since the implantations were carried out at low powers to avoid heating of the irradiated sample.

Results and Discussion

The ^{119}Sn Mössbauer spectra of all of the LTT samples examined in the present study consisted of single resonance maxima at all temperatures. A representative spectrum is shown in Fig. 1. Observed line widths (FWHM) were on the order of 0.79 ± 0.07 mm sec^{-1}, and showed no systematic correlation either with temperature for a given sample or with composition at a given temperature. A representative data set is shown in Fig. 2. Moreover, these line widths indicate that any quadrupole hyperfine interaction at the Sn atom lattice site is well below the resolution limit of the ^{119}Sn Mössbauer technique, and thus that departure from cubic charge symmetry around the tin atom must be minimal in all of the samples studied.

The absence of a resolvable quadrupole hyperfine interaction in LTT is somewhat surprising, both in view of the reported (*1*) rhombohedral distortion (α = 89.88°) in SnTe at temperatures below ~160 K, and the ^{119}Sn Mössbauer data (*7, 17*) of *p*-type SnTe, which appear to indicate that the low temperature spectra are better accounted for by a two line fit. In this context it is also worth noting that the 77 K data for SnTe, reported in an extensive survey (*18*) of tin intermetallic systems, showed an unusually large line width (1.30 mm sec^{-1}), although in the absence of experimental details concerning absorber thickness and sample preparation it is difficult to ascribe this result unambiguously to a low temperature quadrupole splitting in tin telluride.

Moreover, a resolvable quadrupole hyperfine interaction might have been expected for the $Pb_{1-x}Sn_xTe$ samples with a high Pb : Sn ratio (e.g., x = 0.21, 0.25) since on the average, every unit cell including a tin atom will have at least one neighboring unit cell with a lead atom. In view of the difference in atomic (ionic) radii of Sn and Pb, it might have been expected that a lattice distortion from simple cubic symmetry

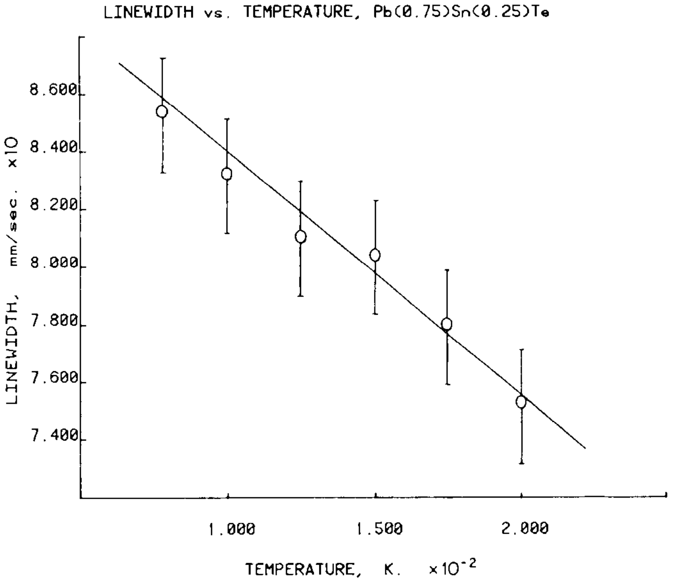

FIG. 2. Full width at half maximum of the ^{119}Sn Mössbauer resonance in $Pb_{0.25}Sn_{0.75}Te$. The large value of this parameter for the liquid nitrogen temperature point is an instrumental effect associated with transfer of liquid cryogen to the sample cell. No evidence for systematic temperature dependent line broadening has been extracted from these data.

around the tin atom would arise in these matrices. If such a distortion is, in fact, realized in these lattices, the resulting field gradient at the tin atom crystallographic site is too small to be resolved by the ^{119}Sn Mössbauer measurements.

The isomer shift data of the LTT samples examined in the present study are summarized in Table I. The 78 K value appears to be independent of x and has a mean value of 3.478 ± 0.013 mm sec^{-1}. This isomer shift (relative to SnO_2) is nearly identical to that reported (*6, 18, 19*) for SnTe and is typical of tin (II) chalcogenides in which there is appreciable covalent character in the tin–ligand bonding interaction. The similarity in the isomer shift between $Pb_{0.8}Sn_{0.2}Te$ and SnTe has been observed previously (*20*) and is indicative of the fact that the nearest neighbor bonding environment of the Sn probe atom remains unaffected by replacement of Sn by Pb in the next unit cell(s) of the matrix. The temperature dependence of the isomer shift for all of the LTT samples lies in the range $(2.9 \pm 0.5) \times 10^{-4}$ mm sec^{-1}. This value is comparable to the corresponding data reported (*6, 17, 18*) for SnTe, but is larger by almost one order of magnitude than the value calculated by Kuo and Chang (*21*) and the experimental data of Lin (*22*) cited by these authors. A representative data set of IS(T) is summarized graphically in Fig. 3.

As has been noted previously (*23*), a characteristic lattice temperature can be extracted from temperature dependent Mössbauer data and used as a relative measure of the Debye temperature of the matrix. Using the thin absorber approximation, for which the temperature dependence of the area under the resonance curve is equal to the temperature dependence of the recoil-free fraction, leads to a Mössbauer (Debye–Waller) lattice temperature given

TABLE I

SUMMARY OF MÖSSBAUER (^{119}Sn) DATA FOR LTT

Sample x	Pb : Sn	IS(78 K)[a] (mm sec^{-1}) ($\pm$0.020)	$d \ln A/dT$ ($\times 10^3$, K^{-1}) ($\pm$0.050)	cc[b]	M_{eff}[c] amu ($\pm$10)	θ_M[d] k ($\pm$5)	d(IS)/dT ($\times 10^4$, mm sec^{-1} K^{-1}) ($\pm$0.075)	θ'_M[e] K ($\pm$5)
0.21	3.8	3.486	9.829	0.998	167	135	2.497	114
		3.469	9.877	0.993	152	135	2.742	119
0.25	3.0	3.482	10.24	0.999	153	133	2.25	119
0.55	0.82	3.485	9.215	0.994	180	139	2.323	114
0.75	0.33	3.472	9.76	0.999	116	136	3.78	146
		3.471	8.99	0.999	127	141	3.28	137
SnTe[f]	—	3.427	8.70	9.995	183	144	—	—

[a] With respect to SnO$_2$ at 295 K.

[b] Correlation coefficient calculated assuming a linear regression.

[c] Calculated from Eq. 3.

[d] Calculated from Eq. 1.

[e] Calculated from Eq. 4.

[f] R. F. Davis and R. H. Herber, Unpublished results. See also Refs. (*4, 5*) *inter alia*.

by

$$\theta_M = -\frac{1.752\,E_\gamma}{c}\,[M_{\mathrm{eff}} k_B (d \ln A/dT)]^{-1/2} \quad (1)$$

in which E_γ is the Mössbauer gamma ray energy, M_{eff} is the effective mass of the probe atom, k_B is Boltzmann's constant and $d \ln A/dT$ is the temperature dependence of the area under the resonance curve for a thin absorber in the high temperature ($T \geq \theta_M/2$) limit. A representative data set for the temperature dependence of the area under the resonance curve is summarized in Fig. 4. If the effective mass is that of a "bare" Sn atom, use of the appropriate constants in (1) leads to relationship of the form

$$\theta_M = 1.338 \times 10^1[(d \ln A)/dT]^{-1/2}. \quad (2)$$

A more realistic estimate for M_{eff} can in some instances be extracted from the second-order Doppler shift, under the assumption that the major contribution to the temperature dependence of the isomer shift arises from vibrational motion of the probe atom. Under this assumption

$$M_{\mathrm{eff}} = -\frac{3}{2}\frac{E_\gamma k_B}{c\,(d(\mathrm{IS})/dT)}. \quad (3)$$

Using this relationship in (1) leads—in the case of ^{119}Sn Mössbauer data—to

$$\theta'_M = 7.155 \times 10^2\,[d(\mathrm{IS})/dT)/((d \ln A)/dT)]^{1/2}. \quad (4)$$

The calculated values for θ_M and θ'_M are summarized in Table I. Because of the small value of d(IS)/dT and the intrinsically large line widths encountered in ^{119}Sn Mössbauer data, the θ'_M data have a significantly larger error associated with them than is true for the θ_M values, which depend only on the slope of the ln(area) vs temperature data. Neither of these two lattice temperatures show a systematic variation with the compositional parameter x. The mean value for θ_M for all of the LTT samples is 135 ± 3 K, and is essentially identical to the θ_M values reported for SnTe, as summarized in Table II, if the value of 167 ± 3 K

TABLE II

SUMMARY OF LATTICE TEMPERATURE DATA FOR SnTe AND RELATED SOLIDS

Sample	Method	Probe atom	θ_M	Ref.	Remarks
SnTe	Mössbauer	Sn	132 ± 3	*4*	85 ≤ T ≤ 250 K
	Mössbauer	Te	141 ± 5	*4*	
	Mössbauer	I	139 ± 3	*4*	
	Mössbauer	Sn	139 ± 3	*6*	at 290 K
	Mössbauer	Sn	140 ± 6	*29*	
	Mössbauer	Te	141	*5*	
	Mössbauer	Sn	154	*2*	
	Mössbauer	Sn	164	*7, 17*	78 ≤ T ≤ 300 K, linear fit
	X-ray	all	167 ± 3	*8*	
PbTe	X-ray	all	108 ± 3	*30*	
$Pb_{0.63}Sn_{0.37}Te$	X-ray	all	118 ± 4	*8*	

extracted from the X-ray data (*8*) is excluded. A more direct comparison between the X-ray powder pattern data and the Mössbauer data can be effected for an LTT sample with $x = 0.37$ for which θ (X ray) = 118 ± 4 K and samples with $x = 0.21$ and 0.25 for which $\theta_M = 135 \pm 5$ and 133 ± 5 K, respectively. As noted in conjunctions with the X-ray crystallographic data (*8*) and the results of Sternberg *et al.* (*9*), the lattice parameters change by only 2% in going from PbTe to SnTe, presumably due to the small size difference of Pb and Sn (covalent radii 1.40 and 1.46 Å, respectively) in the

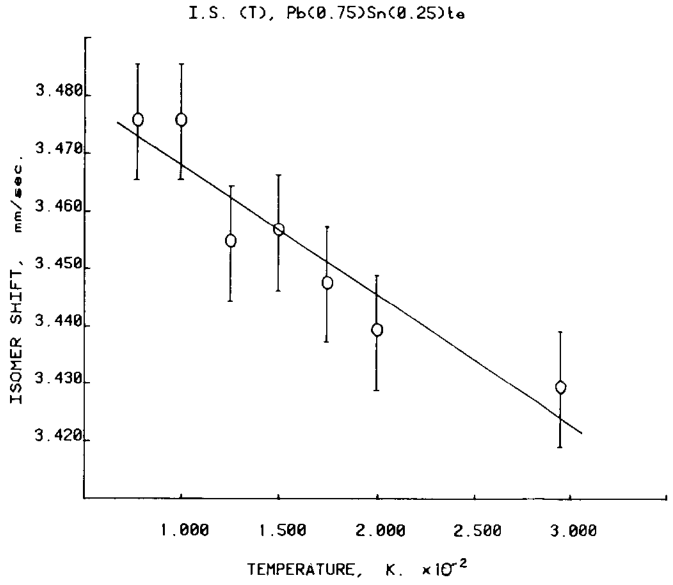

FIG. 3. Temperature dependence of the isomer shift for $Pb_{0.75}Sn_{0.25}Te$ in the range 78 ≤ T ≤ 295 K. The solid line is a linear least squares regression fit to the data with a correlation coefficient of 0.942 for the seven data points.

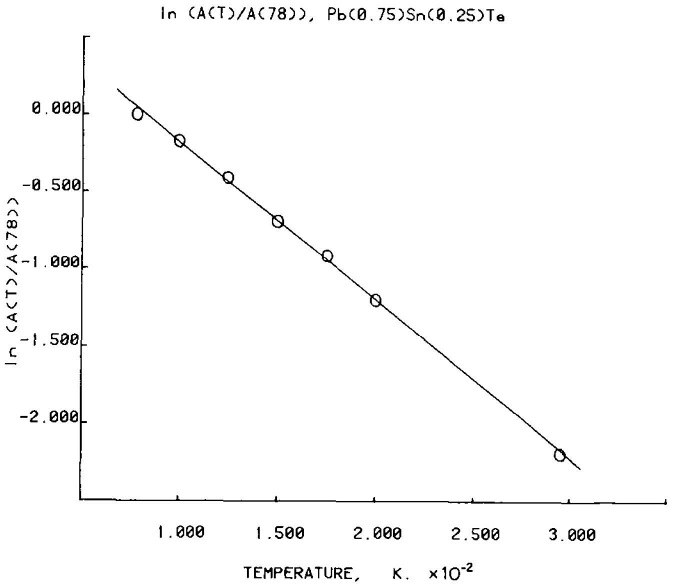

FIG. 4. Temperature dependence of the area under the Mössbauer resonance curve for $Pb_{0.75}Sn_{0.25}Te$. The solid line is least squares regression fit to the data with a correlation coefficient of 0.999 for the seven data points.

electronic configurations encountered in the LTT environment.

Finally, it is worth noting that neither the ln $A(T)$ data, nor the temperature dependence of the line widths of the Mössbauer resonance in $Pb_{1-x}Sn_xTe$ show any evidence for the phase changes reported (*1*, *7*) at ~160 K in SnTe. The rhombic (low temperature) to cubic (high temperature) phase transition in *p*-type SnTe with a carrier concentration of ~0.88×10^{20} cm^{-3} due to Sn vacancies in slightly nonstoichiometric samples has been observed as high as 98 K by neutron diffraction methods (*24*) and as high as 125 K by conductance measurements (*25*), but appears (*26*) to be absent in $Pb_{1-x}Sn_xTe$ ($x = 0.21$ to 0.35) with carrier concentrations of 0.68 to 300×10^{17} cm^{-3}, although a ferroelectric phase transition in such materials has been reported (*26*). The strong dependence of the transition temperature on carrier concentration in LTT has been noted in a recent (*27*) study, but no evidence for a lattice instability and the accompanying softening of the transverse optic phonon mode is evident from the Mössbauer lattice dynamical data of the present investigation.

It is also clear from the present data that the large line broadening effects near 190 K, which are observed (*28*) in the $Sn_{1-x}Ge_xTe$ ($x < 0.1$) system, are not evident in the LTT samples examined in the present study. An extension of the concentration range to more nearly match those reported by Fano *et al.* (*28*) may be required to elucidate the differences in the two systems more fully.

Radiation Damage Experiments

In an extension of earlier studies (*15*) of the radiation damage produced in $NbSn_3$ by 2-MeV proton bombardment, an attempt was made to study the effects of such treatment on the lattice dynamical properties and hyperfine interaction parameters of LTT. Since the damage induced by the protons, and not their doping effect, were the subject of the present study, the LTT thickness and damaging beam energy were chosen such that the proton range slightly exceeded the LTT target thickness, taking into account the 45° orientation of the sample with respect to the proton beam. Two samples were investigated in detail. In the first of these experiments the thin absorber of $Pb_{0.25}Sn_{0.75}Te$, which had been used in the earlier studies (*vide supra*), was irradiated with 2-MeV protons to a total fluence of $\sim 10^{17}$ cm^{-2}. The irradiation was carried out with the target nominally at liquid nitrogen temperature, but the sample was allowed to warm to room temperature prior to mounting in the Mössbauer spectrometer for subsequent study. In the second experiment, a sample of the $Pb_{0.79}Sn_{0.21}Te$ absorber (*vide supra*) was similarly irradiated with 2-MeV protons, but subsequently mounted in the Mössbauer spectrometer without warming to a temperature in excess of ~150 K.

The Mössbauer spectra of these samples at liquid nitrogen temperature did not evidence any anomalous resonance absorption at a line position other than that observed in the unirradiated samples. The 78-, 120-, 180-, and 232-K spectra of the irradiated $Pb_{0.25}Sn_{0.75}Te$ were examined for excess line broadening of the absorption maximum, such as that observed in the earlier study (*15*) of Nb_3Sn or in the α-irradiation studies of SnTe by Ambe and Ambe (*3*). No evidence of such broadening was observed, and the calculated line widths were well within the error limits (± 0.02 mm sec^{-1}) of the data for the unirradiated sample indicated in Table II and Fig. 2. Moreover, the data for the temperature dependence of the recoil-free fraction in both irradiated samples agreed well with the corresponding values for the unirradiated absorbers, and no significant change in either θ_M or θ'_M was evidenced in these experiments.

The results strongly imply that the effects of 2-MeV proton irradiation of LTT are sufficiently well annealed—even at 150 K—that no residual effects of such treatment persist in the lattice, at least to the extent that these can be probed by the ^{119}Sn Mössbauer techniques used in the present study. This conclusion is in agreement with the results on proton and alpha particle bombarded ^{120}SnSb and ^{120}SnTe observed (*3*) in absorption experiments and the computer simulations of radiation damage in such matrices. While it is possible that nonsubstitutional lattice positions for the ^{119}Sn probe atoms may remain stabilized at lower temperatures, the present experiments show that such anomalous site defects cannot be observed directly, or by the effect on the lattice dynamical properties of the LTT host matrix, with the techniques employed in this study.

The present results are in accord with the conclusions about the nature of the damage in heavy ion implanted LTT deduced from channeling measurements (*12*). The Rutherford backscattered channeling spectra do not show damage peaks typical for point defects but are dominated by dechanneling, presumably caused by extended defects. Such defects, which are typical for damage in irradiated metals, are not expected to be readily observable by transmission Mössbauer experiments as only a few atoms in the defect region are localized in a strongly disturbed environment. The fact that even for the sample, which was not allowed to warm up above ~150 K, no irradiation effects were evident may indicate that already at such temperature only extended defects prevail in damaged lead tin telluride.

Acknowledgments

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