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Sn-119 Mössbauer study of dilute tin-lead alloys

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Mössbauer spectroscopy has been performed using the ^{119}Sn resonance on a variety of low-concentration tin in lead samples, ranging from 1.3 at. % to 18.5 at. % tin in lead. We observe three basic resonances, which we identify as dispersed tin in lead (I), precipitated β (white) tin in lead (II), and precipitated α (gray) tin in lead (III), where the latter is only observed below 286 K. Contrary to earlier published results that reported an anomalous falloff in the elastic fraction for dispersed tin in lead, we find only the typical temperature dependence. The Mössbauer temperature is found to be 104 K for the dispersed state, as found from a Debye model analysis based on the transmission integral. Both this Mössbauer temperature and the isomer shift relative to a $CaSnO_3$ source agree with earlier published values within experimental error. For the precipitated state (II), it is found in the initial stages of precipitation both the isomer shift and the measured Mössbauer temperature are close to that of the dispersed state (I). As the sample is annealed or cold worked, the precipitates grow and both the isomer shift and the characteristic Mössbauer temperature approach that of β-Sn, 140 K. The precipitation-dissolution reaction is traced using a sample containing 18.5 at. % tin in lead by annealing at progressively higher temperatures and following changes in the isomer shift. Dissolution is found to begin as low as 360 $(+15/-5)$ K. A significant result that has not been reported by earlier investigators of this system is the observation using Mössbauer spectroscopy of the α phase of tin (III). Furthermore, the formation of this phase takes place without the usual long incubation period required when a lead host matrix is not used. Moreover, a technique for curve fitting such Mössbauer spectra based on an analytic expansion of the transmission integral is demonstrated that isolates each component in the unresolved resonance. We find that the Mössbauer effect technique can be used for assessing the phase diagram in systems such as the Sn-Pb alloy, and our results indicate that the accepted phase diagram may need refinement. [S0163-1829(98)05034-6]

I. INTRODUCTION

Throughout the past century the tin-lead system has been studied quite extensively, as is summarized by Karakaya and Thompson.[1] The experiments that measure the low-concentration solubility of tin in lead are illustrative of the practical uses of tin-lead alloys, for these alloys are widely used as solders in the microelectronics industry. Due to the fact that high electrical current densities could possibly lead to the undesirable thermomigration or electromigration of tin atoms along grain boundaries, the mechanism of coupling of precipitates to the host lattice is of great interest.[2] For example, a relatively small precipitate would be expected to closely resemble the solution state in a bulk material, in which case the lattice coupling to the small precipitate is expected to be similar to that of dissolved impurities in the host lattice.

Another area of general interest is the performance of a tin-lead solder alloy under extreme temperature conditions, such as may be encountered in an arctic defense or aviation application. In fact, tin is known to undergo a phase transformation at a temperature of 286.2 K.[3] In this transformation, it goes from the ductile body-centered-tetragonal β phase (white tin) at higher temperatures to the rather brittle diamond structure α phase (gray tin) upon cooling. While there is some question as to whether the transition is martensitic or first order in nature, most sources in the literature believe it to be the latter.[3–6] The point is that the slow kinetics at the transformation temperature require an essentially diffusionless transition.

All of the work noted in the above summary and most work present in the literature use such techniques as electrical resistivity and bulk calorimetry to study the properties of the lead-tin alloys. In addition, scanning electron microscopy (SEM) and transmission-electron microscopy studies of the $\alpha\leftrightarrow\beta$ transformation are quite common. In these studies, large scale changes such as the precipitation-dissolution reaction can be tracked from their initial to final states fairly easily. On the other hand, these techniques are not very useful in examining possible intermediate states that might occur during the process. Because certain Mössbauer effect (ME) parameters such as the recoil-free fraction f and the characteristic Debye temperature θ_D depend on the coupling to the host lattice of the probe, ^{119}Sn Mössbauer spectroscopy is an excellent technique for studying the details of the tin-lead system, and in particular the precipitation-dissolution reaction and phase transformations. In this manner microscopic changes in the tin-lead alloys such as precipitate particle size effects should be observable, while they are not visible with macroscopic techniques. It should be noted that Debye temperatures found from ME data are somewhat different than those determined from heat-capacity measurements. Each involves a different weighting of the Debye density of phonon states, which is used as an approximation to the actual density of states. All characteristic Mössbauer temperatures shall be denoted as θ_M in this paper.

The precipitation-dissolution reaction in the tin-lead system has been examined earlier using Mössbauer spectroscopy by Arriola and Cranshaw.[7] They tracked the center shift and the area of the ME resonance as seen in an 8 at. % tin in lead sample as a function of sample temperature. They observe a temperature dependence of the recoilless fraction that includes a sharp transition as the sample temperature is raised and the precipitates of tin dissolve into the host lead matrix. However, a much more accurate and complete analysis can be performed using the correct curve fitting techniques outlined below. In addition, a procedure for the accurate fitting of multiple lines in a single unresolved spectrum can be developed. This situation will always be encountered in samples containing a mixture of tin in the precipitated and dilute states, as well as tin in the α and β phases, and thus a fitting technique is needed to completely characterize the Mössbauer spectra.

This research was originally motivated by a desire to verify and further investigate a surprising Mössbauer result reported by Shechter, Stern, Yacoby, Brener, and Zhang (SSYBZ) in 1989.[8] Specifically, these researchers presented remarkable Mössbauer data taken using several samples of lead doped with very small concentrations of tin, ranging from 0.5 to 5 at. %. They report a rapid falloff from the usual Lamb-Mössbauer behavior exhibited by solids, at a critical temperature of 150 K for their 1% tin in lead sample. While the $f(T)$ curve is similar in appearance to that found by Arriola and Cranshaw, the results are interpreted by SSYBZ as resulting from isolated premelting around Sn impurities. Since this premelting takes place at a temperature of about 25% of the bulk melting temperature of the host, this apparent result is very surprising. They cannot explain their data by the precipitation-dissolution mechanism in that the diffusion rates are too low at 150 K. We have repeated this interesting experiment but were unable to confirm the SSYBZ result. This will be discussed in detail in Sec. V.

In the absence of any perturbing effects such as interference, the energy profile of the radiation emitted by a decaying nucleus (and, of course, absorbed by an absorbing nucleus) will follow a Lorentzian line shape. In practice, however, perturbations such as finite source and absorber thicknesses are almost always present. Moreover, due to the complicated nature of fitting to the exact transmission integral, it has always been widespread practice to analyze Mössbauer data using just a simple Lorentzian line shape with the linewidth as an empirical parameter. When fit to a Lorentzian line shape, though, spectra taken on samples outside the thin source and absorber limits always return incorrect parameters. Furthermore, in an actual Mössbauer experiment, the signal seen at the detector is in fact a convolution of the source and absorber line shapes. The actual functions for typical source and absorber thicknesses are highly modified from Lorentzians, because of such effects as saturation, interference, and source resonance self-absorption (SRSA). As more factors are worked into the analysis, the source and absorber functions become extremely complicated. In practice, therefore, the transmission integral representing the true line shape is very difficult to evaluate in a reasonable amount of calculational time. Mullen *et al.*[9] outline a procedure whereby the source and absorber terms in the transmission integral are expressed as an analytic series using Fourier transforms, which in this case are rapidly converging. When programmed into a computer, Mössbauer line shapes can then be fitted to arbitrary accuracy using well-known least-squares fitting techniques. Thus, one can completely and accurately determine important line-shape parameters such as the thickness numbers (proportional to the recoil-free fraction f), interference parameters, linewidths, and line positions.

In summary, the Mössbauer effect using ^{119}Sn can be used to study the mechanisms involved in the precipitation-dissolution reaction in a tin-lead alloy. Specifically, the microscopic precipitates likely to be present in the initial stages of a reaction should have a unique signature in a Mössbauer experiment, while said precipitates cannot be seen with the other techniques mentioned above. By fitting Mössbauer data to the transmission integral, the presence of tin in the α phase was detectable in our experiments, even though it was not found in the earlier ME studies of this system.[7,8] In addition, the ME technique can be used as a probe of the tin-lead phase diagram, as we show for a sample of lead with 18.5 at. % tin. Finally, we shall demonstrate that fitting Mössbauer data to Lorentzians in any regime outside of the ideal thin limit is inherently flawed and leads to erroneous characteristic temperatures and other discrepancies.

II. BACKGROUND

In a well-known result, the slope of a plot of the natural logarithm of the recoil-free fraction f vs temperature in the high-T region should be

$$s=\frac{-3\hbar^2k^2}{mk_B\theta_M^2}, \tag{1}$$

where $\hbar$ is Planck's constant divided by 2π, k is the magnitude of the wave vector of the outgoing radiation quantum, m is the mass of the Debye oscillators, k_B is the Boltzmann constant, and θ_M is the effective characteristic Mössbauer temperature of the lattice. Thus, we would expect that such a plot would yield a generally linear plot for $T>2\theta_M$, with an inverse squared dependence on the characteristic temperature. However, the magnitude of this effective characteristic temperature will depend on the physical situation present at the sites of the Mössbauer atoms, i.e., either isolated substitutional impurities or precipitates at the grain boundaries, for one would expect different couplings to the host lattice in each situation. Finally, we would expect deviation from this Lamb-Mössbauer behavior for a specified environment only at very high temperatures where anharmonicity effects make large contributions. In such a case the recoilless fraction would falloff much more rapidly than the case of the common harmonic approximation used in the derivation of Eq. (1).

Another feature of a Mössbauer resonance that bears mention at this point is the isomer shift. This shift is caused by a Coulombic interaction between the atomic s-shell electrons and the charged nucleus of an atom, and it thus results in the actual resonance being shifted in energy by a small amount commonly noted as δ. However, the dependence of the isomer shift on the electron density at the nucleus leads to a fairly unique signature of the various oxide states of tin. Furthermore, the isomer shift is expected to be different for isolated impurities in a host material and precipitates large enough to reflect the properties of their bulk constituency.

Thus, the isomer shift also can aid in assessing the microscopic nature of tin precipitates and dispersed tin in lead.

III. DATA ANALYSIS

In a Mössbauer experiment using transmission geometry, the actual signal observed at the detector will be a convolution of the source and absorber terms. Unfortunately, there is no closed form analytical expression for this convolution integral. It can be treated, however, with an exact and rapidly convergent analytic representation due to Mullen *et al.*[9] This methodology expands both the source and absorber terms in a power series in the source and absorber resonant thickness numbers using a Fourier transform method. In this manner the spectrum is completely defined using these parameters: v_0 the peak centroid, Γ the natural linewidth, C_0 the off-resonance background, f_s the source recoiless fraction, t the absorber resonant thickness number, β the interference parameter, and t_{rs} the source resonant thickness number. When programmed into a computer the analytic expression thus permits accurate determinations of the above fundamental parameters. Furthermore, in the case of ^{119}Sn, the interference parameter is taken to be negligible as predicted theoretically, and the source resonant thickness number t_{rs} and natural linewidth Γ from earlier precision measurements are independently determined and inserted into the fitting functions as constants, rather than parameters to be determined. The thickness number t is a dimensionless gauge of thickness equal to the product of the number of Mössbauer absorbing atoms per unit area times the resonant cross section times the recoilless fraction ($t = n\sigma_0 f$).

The data analysis techniques are not quite as simple in the cases where the Mössbauer signal is coming from two or more components, arising from alternative possible environments. One would expect that any small precipitates present containing the Mössbauer isotope would couple to the host lattice differently than in the isolated impurity case, and thus, they should then have a different δ and effective θ_M. Also, this θ_M would be different than that of a macroscopic sized crystal of the precipitate state embedded in the solid. More significantly, we would expect differences in atomic electron densities at the precipitated Mössbauer nuclei due to said nuclei no longer being substitutional impurities, causing a change in the isomer shift of the resonance. This effect would be further enhanced in the cases where the precipitates have a different crystal structure than the host lattice. The Mössbauer signal will now no longer be a single line, instead becoming two or more lines which for ^{119}Sn in Pb are mostly unresolved and visually appear as a broadened line. This can easily be seen by fitting the spectrum to the analytic representation of the line shape and examining the residual plot and the χ^2 value found for the fit. The residual plot will show a characteristic pattern due to the fitting function failing to account for the extra resonance and the χ^2 will be significantly higher than that encountered after a good fit to a true single line. Finally, as the size of the precipitates increases and they begin to take on the characteristics of the bulk material, which in the present experiment is α or β tin, one would expect the isomer shift to approach the value for this bulk material as the signal from the precipitate begins to dominate that from the remaining isolated impurities.

In the experiment described herein, three distinct Mössbauer resonances were found, associated with dispersed tin in lead and with two types of precipitates of tin. All three of these resonances were unresolveable to immediate visual inspection, but they were easily identifiable by curvefitting with the analytic expansion of the convolution integral.

The curve fitting techniques outlined above can be extended to the case of structured spectra, i.e., split and multiple lines. The apparent splitting can come about from any of several mechanisms, such as electromagnetic field gradients, magnetic hyperfine interactions, or just the presence of multiple single-line resonances in the sample. In the present case, the extra lines will be coming from Mössbauer resonances that can be treated independently. In this case the transmission integral can be written as a sum of the transmission integral for a single-line spectrum. The spectrum is then fit by adding up the separate fitting functions representing each resonance so as to yield the entire spectrum.

IV. EXPERIMENTAL METHODS

For this experiment the source material used was calcium stannate, Ca^{119}SnO$_3$. Fabricated by the Amersham Corporation, it contained 1.42×10^{-6} g of radioactive isotope with an initial activity of 5 mCi. It was mounted in a cryogenic source holder with a effective diameter of 14 mm and the calcium based matrix gives an *f* value of close to 0.7 at room temperature. Furthermore, the line is unsplit and the linewidth is near the ideal limit ($\Gamma = 0.32$ mm/s) for a fresh, carrier-free source. When the data was analyzed these values could be put into the fitting functions as known quantities, thus avoiding problems with variable correlation.

As any source ages and decays, Mössbauer atoms in the ground state must build up in the source itself. Since they will always be in resonance with the desired radiation, significant SRSA can take place, creating an extra broadening in the Mössbauer line.[10] This effect, however, can be taken into account in most fitting functions if an accurate source resonant thickness number can be found.[9] This was determined by simultaneously fitting four spectra of the same sample taken at different temperatures and constraining the absorber thickness numbers to follow the empirical temperature dependence of the Lamb-Mössbauer factor. A source resonance thickness number (t_{rs}) value of 0.5 was returned, and henceforth used in all fits. Although t_{rs} can change considerably with time large cross-section isotopes, this effect was not important over the period in which the data runs reported herein was taken. The source electronic thickness number T_{es} was calculated to be 0.267 by considering the physical dimensions of the radioactive material and the (sealed) source holder.

The data was gathered with a multichannel scaler. Velocity scans were achieved via the use of an electronic transducer with a feedback controlled drive operated in the sinusoidal mode. The transducer velocity was calibrated periodically using the well-known line positions of the ^{57}Fe Mössbauer resonance. Both a silicon-lithium drifted [Si(Li)] and a solid-state germanium detector were used interchangeably, depending on which was available for service during a particular data sequence. Both have efficiencies close to

100% at the energy of the Mössbauer transition of interest.

In order to accurately control the absorber temperature, the samples were mounted in a Janis ST-4 continuous flow cryostat. The sample holder itself consisted of a copper block, to which the sample foils were held in between two thin pieces of either transoptic disk or boron nitride by a copper mounting collar. The disks were used purely to maintain sample rigidity. The cryostat could then be operated using the vapor of either liquid helium or liquid nitrogen as a coolant. The coolant is transferred via an evacuated transfer line from a storage dewar held at a pressure of 4 psi by means of a popoff valve, and either vented into the atmosphere after flowing through the cryostat (nitrogen) or recovered (helium). Four psi was found to be the best compromise between adequate flow rate and flow rate controllability.

Most experiments usually require separate pieces of sample apparatus to make data runs above and below room temperature. To examine this whole range would require the sample to be removed from a furnace, for example, and then remounted in a cryostat. This could lead to geometrical differences in the experimental setup that would then change the background counting rate, and thus could prevent direct and simple comparison of the hot (above room temperature) and cold (below room temperature) data. In order to prevent the above difficulty, the Janis cryostat was outfitted with materials capable of withstanding both hot and cold temperature operation. It thus had an effective temperature range from 475 K down to liquid-helium temperatures. The temperature sensor, mounted in the sample block, was of the silicon diode type and, in fact, this sensor is what created the upper temperature bound for the system as a whole.

Extreme care was taken in producing homogeneous ^{119}Sn in Pb samples. Obviously, all of the experimental constituents must be present in the final product in their premeasured and desired amounts, i.e., one element does not leech into any container used in the manufacturing process or vice versa. Also, composition modifications due to evaporation must be minimized. If either were to occur in a significant way, the desired concentration would be altered. Also, one must control extraneous impurities in general (for example, oxides of tin are easily formed, although they are readily visible in a Mössbauer spectrum and can be extracted in the data analysis).

To best alleviate these problems, several steps were taken. First, the samples were produced in as inert an environment as possible. This included forming the actual ingot in a small crucible made of Macor, a commercially available material that worked well for us, while alternative crucibles did not. Platinum was used for the retaining clips for the holder. All parts were thoroughly cleaned before use, and the heating was done under a hydrogen atmosphere, the hydrogen having first been filtered through a device designed to remove any traces of oxygen. The sample was held at approximately 500 °C in the furnace for about five days, and agitated at least three times a day. Finally, the sample was water quenched while still under the hydrogen atmosphere immediately upon removal from the furnace.

The samples were all easily removed from the Macor crucible, and usually they could be ''poured.'' Hence, chemical interactions with the crucible itself were not a problem. Many of the samples were reweighed immediately after removal from the furnace. In all cases nearly 100% recovery was achieved, with the worst case being 99%. If the missing mass was indeed tin in these cases, this would not be a desirable situation because of the lead-rich nature of the samples. However, no evidence was ever found that one element was preferentially disappearing during the manufacturing process. Furthermore, several samples were prepared for analysis by both the Materials Science and the Earth and Atmospheric Science departments at Purdue, containing from 1 to 5 at. % tin in lead by initial weight. These samples were analyzed under both a SEM and under an optical microscope equipped to take photographs. Upon examination, no tin-rich regions could be found in the low-concentration samples, showing the tin to be homogeneously dispersed into the Pb matrix. The higher-concentration samples were quite different, having easily identified pure tin regions homogeneously distributed throughout the sample. These regions ranged in size from approximately 5 μm across down to about 1 μm, which was the smallest that could be unambiguously identified. The most important consideration, though, is the observed homogeneity of the precipitates. These samples were also checked using wavelength dispersive spectroscopy, which confirmed the ratios of tin to lead in our samples were the same as in our starting materials to within machine error.

After the samples were prepared in the above manner, they were placed between two pieces of stainless-steel shim stock, which had been previously cleaned. They were then rolled in a small hand-operated rolling press, with the rollers clamped down slightly more with each pass. By rolling the sample a little thinner each time and changing pieces of shim stock approximately every four passes, the problem of the soft lead sticking to the shim stock could be usually alleviated, although the technique required practice to avoid sample damage. Using this methodology, a thickness of less than 25 μm could be attained.

V. RESULTS AND DISCUSSION

A. Results for slightly doped samples

As an initial data run, four samples ranging in Sn concentrations from a low of 1.3 at. % to a high of 5.4 at. % were analyzed. Mössbauer data were taken over a wide temperature range, from 4.5 K to slightly higher than room temperature. The results from the 1.3 at. % case are shown in Fig. 1. For comparison purposes we also show the results reported by SSYBZ by dashed lines in Fig. 1. In Fig. 2 we show the data for four low-concentration samples. This data was used to calculate the Mössbauer characteristic temperature for each of these measurements and the result of this calculation is given in Table I. A more detailed presentation of this data with Mössbauer and residual plots can be found in the Ph.D. thesis of Scott N. Dickson, Purdue University, 1995.

The Mössbauer temperatures were obtained by fitting the data to the analytic form of the transmission line-shape function, and then fitting the returned natural logarithm of the Mössbauer thicknesses t (proportional to f) to the Debye integral as described in Sec. I.

Although only the 1.3 at. % case is shown in Fig. 1, all the data follow a similar well-defined Debye-model curve over the experimental temperature range, as seen in Fig. 2.

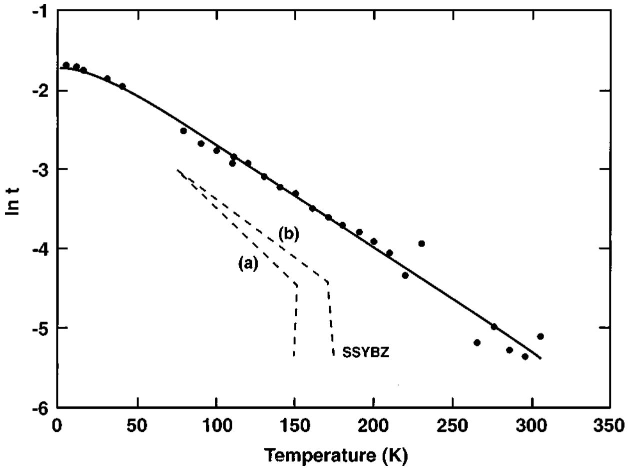

FIG. 1. Natural logarithm of the Mössbauer thickness number *t* vs temperature *T* for a 1.3 at. % sample. The dashed curves (*a*) and (*b*) give an approximate representation of the SSYBZ data from Ref. 8 for their 1% and 2% samples, respectively. In this representation we have arbitrarily shifted the vertical and assumed that their intensities are proportional to our thickness number *t*, which is approximately true.

The returned characteristic temperatures of 104(2) K, 104(2) K, and 107(2) K for the 1.3, 1.6, and 3.0 at. % samples, respectively, agree well with values published by Andreasen *et al.*[11] in the dilute alloy cases. They report a value of 113 K, using Lorentzian fits to their data. The fact that the three samples ranging from 1.3 to 3.0 at. % return the same value for θ_M within experimental error can be taken as evidence that the ^{119}Sn is in the same lattice environment in each sample. The Mössbauer temperature of 118(2) K for the 5.4 at. % Sn in Pb sample reflects the presence of larger precipitates in this more highly doped sample, which is clearly above the precipitation limit. The Mössbauer signature of precipitates in an otherwise pure host matrix is discussed later.

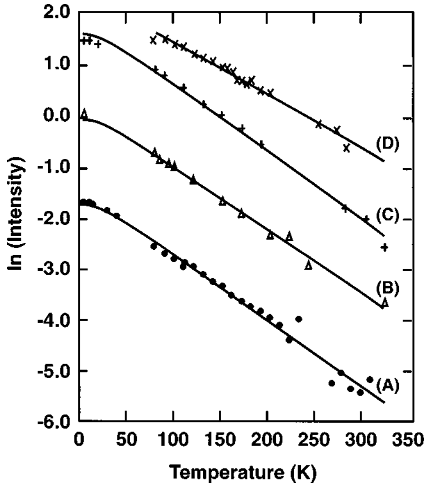

FIG. 2. Natural logarithm of the integrated intensity taken to be proportional to the thickness number *t*, fit to the Debye model. Curves (*A*) through (*D*), respectively, represent tin in lead concentrations of 1.3, 1.6, 3.0, and 5.4 at. % and have been displaced on the vertical axis for the purpose of comparison. The slope of curve *D* is significantly less than that of *A*, *B*, and *C*, indicating a higher Mössbauer temperature for the 5.4% sample.

TABLE I. Calculated Mössbauer temperatures from the initial data run. The number in parentheses represents the estimated statistical error in θ_M for each case.

at. % ^{119}Sn	θ_M (K)
1.3	104(2)
1.6	107(2)
3.0	104(2)
5.4	118(2)

In none of the data is there any evidence of a sudden, precipitous falloff from the Debye-Waller behavior as reported by SSYBZ. Their data, as presented in Refs. 8 and 12 and sketched for comparison purposes in Fig. 1, was interpreted as the result of an isolated premelting phenomenon taking place around tin impurities. While possible premelting is indeed a fascinating physical phenomenon to contemplate, the premelting SSYBZ are proposing takes place a full 450 K below the bulk melting temperature of Pb. Furthermore, in a recent paper,[13] Yang, Lu, and Wang find that surface melting in Pb occurs at $T = 520$ K. Roughly speaking, the atoms at a surface will have only half as many bonds as the inner atoms, and thus one would expect melting to occur at a surface at lower temperature than in the bulk solid. This result does not support the model presented by SSYBZ.

Another facet of the SSYBZ model that warrants discussion is the estimated size of the liquid bubble they postulate to surround the Sn impurity. For a 2% sample, for instance, a bubble containing 50 atoms must overlap with the bubble surrounding the next-nearest Sn atom. Thus percolation would manifest itself in a bulk sample as a much reduced resistance to shearing stress, an effect that has never been observed. Depending on the exact size of the bubble, the bulk sample itself would even behave as a liquid. In sum, there are several difficulties with the premelting model proposed by SSYBZ.

The SSYBZ work has been questioned by other researchers, as well. In a 1991 paper,[14] Martin and Singer describe a computer simulation of the behavior of isolated point defects in a model crystal near melting. Using an inverse-6 soft-core model, they fail to observe any premelting near any of the types of defects they simulated (vacancies, polyvacancies, or impurities). Hence, they too are unable to explain the SSYBZ data by premelting.

The SSYBZ data as presented[12] has only two points below the bend in the curve and shows no apparent Mössbauer signal in their 1 at. % sample at the lowest measured temperature (150 K), in which case an intensity cannot be calculated. However, this is in direct contrast to our small concentration samples, for which the signal persisted to room temperature and beyond as seen in Figs. 1 and 2. Furthermore, these measurements indicate that samples containing 3 at. % tin or less are dispersed and do not show a sudden falloff in $f(T)$ as the temperature rises. Our 5.4 at. % sample, on the other hand, has a distinctly lower slope to the ln *t* vs *T* curve, as shown in Fig. 2.

To date the origin of the SSYBZ anomaly remains a mystery. We were unable to duplicate the effect in any of our dilute samples. In fact, we only produced a similar effect in a quite highly doped tin in lead sample as seen in Fig. 3 and

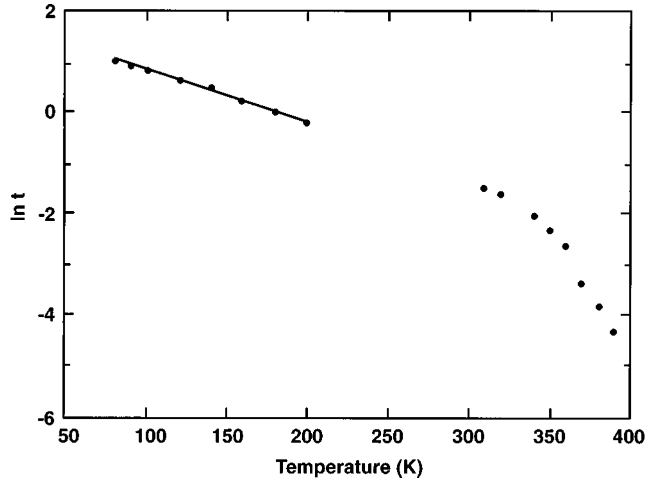

FIG. 3. Natural logarithm of the Mössbauer thickness number t vs temperature T for a sample containing 18.5 at. % tin in lead. Note the obvious deviation from linearity as the precipitation reaction takes place.

discussed below, in which case the precipitation-dissolution reaction is clearly evident in the Mössbauer data.

B. Characterization of precipitated samples

Several samples were examined that were well above the precipitation limit at all but the highest temperatures attainable with our experimental apparatus. By varying the temperature of the sample, various fascinating aspects of the Mössbauer signature of the precipitation-solution reaction could be studied. Using the furnace to hold the samples at high temperatures, the tin could be dissolved into the lead matrix. However, these temperatures were usually too high to observe a Mössbauer effect because of the very small recoilless fraction, and thus a method was needed to obtain a spectrum characteristic of the dissolved state. This was accomplished by rapidly quenching the samples to liquid-nitrogen temperature (with a total time constant on the order of 10 min) and then taking the spectrum. In this manner the high-temperature state was ''frozen'' into the (now supersaturated) sample. With the small exception of a slight reprecipitation in some samples due to the finite time required for the quench, this method worked quite well. In fact, the returned fit parameters of highly doped samples obtained in this manner matched those of previously examined dilute samples.

When curve fitting the Mössbauer data from a slightly precipitated sample to a single line, the signature of these small precipitates can be taken to be the inability to generate a good fit, i.e., the returned value of χ^2 is much greater than one. Conversely, in this case the measured Mössbauer temperature is very close to the dilute case. We measured the Mössbauer temperature for a 5.4 at. % sample both before and after freezing in the high-temperature dilute state as described above. The returned values of θ_M were 114 K and 107 K, respectively. The only difference was an inability to fit the preanneal data to a single line.

C. Basic characterization of large precipitates fit to a single line

The presence of large precipitates of tin in lead can produce some rather dramatic effects in Mössbauer work, especially in the measured Mössbauer temperature and the obvious error signal when performing single-line data fits. In order to illustrate the effects of these large precipitates, a sample containing 18.5 at. % tin in lead was prepared, and a series of Mössbauer spectra were taken as the temperature was increased in progressive increments beginning at 80 K and ending at 200 K. This data yields a θ_M of 130.5 K. Moreover, all of the data fall on the curve within error and there are no anomalous points. Thus, when fit to a single line, the measured Mössbauer temperature of large precipitates of tin in lead is much closer to the characteristic θ_M of pure tin, 140 K. Furthermore, the measured single-line isomer shift is very close to the value for β tin.

Once the Mössbauer temperature was established for the highly precipitated 18.5 at. % sample in the 80 to 200 K region, higher-temperature data were taken. The natural log of the Mössbauer thickness is plotted as a function of temperature in Fig. 3. As the tin precipitate dissolves into the lattice, note the obvious deviation from linearity. The bend in the curve occurs at the temperature at which the signal from the isolated impurity begins to dominate, for the Mössbauer temperature of dispersed tin in lead is much lower than that of large precipitates. Notice the similiarity to the SSYBZ data, shown in Fig. 1. In this case, though, the bend in the curve clearly comes about due to the precipitation-dissolution reaction. The data is presented up to the point at which the temperature was high enough that the Mössbauer resonance could no longer be easily observed due to the reduction in the recoil-free fraction. If higher-temperature data had been gathered, one would expect the $\ln t$ vs T curve to once again become linear, although now the measured θ_M would correspond to the isolated impurity case.

D. Precipitation at lower temperatures

To investigate precipitation at lower temperatures, the 18.5 at. % sample was chosen because its quite high tin content could lead to relatively rapid precipitate particle formation. First, it was annealed for a day at 450 K. It was then rapidly quenched to 80 K, while still in solution and spectra were taken every 20 °C from 80 K up to 240 K. This data is shown as the lower curve in Fig. 4, and a fit to the Debye integral yields $\theta_M = 110.0$ K, showing the tin in the sample to indeed be mostly in solution. As the temperature reached 260 K, however, the fit to that spectrum yielded a value of the thickness number which was clearly above the previous curve by a large increment. The sample was immediately quenched to 90 K, and Mössbauer spectra taken again every 20 °C. The result was the upper curve in Fig. 4, a rather dramatic demonstration of precipitation. Fitting the data on the upper curve to the Debye integral yields a Mössbauer temperature of 127.8 K, a value very close to the previously measured precipitate state value of 130.5 K. The large thermodynamic excess of tin in solution in this sample while cold evidently lets the precipitation reaction take place at temperatures where the kinetics, i.e., the interatomic jump rate, is still relatively slow ($D \cong 10^{-12}$ cm^2/s). Again, because of the high tin doping, a precipitating cluster can grow fairly quickly. Earlier measurements of the same type on lower tin concentration samples (5.4 at. % and lower) did not

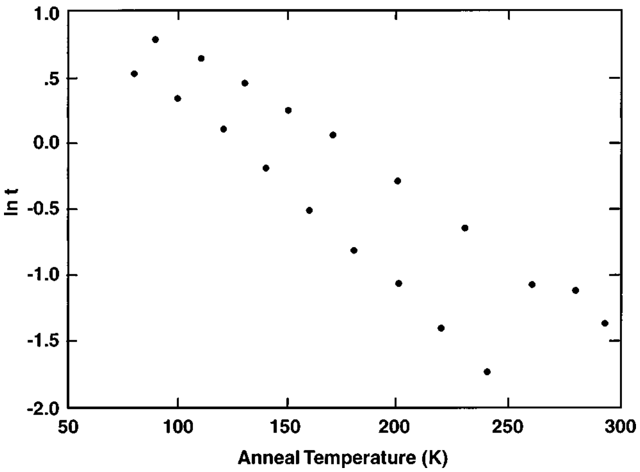

FIG. 4. Precipitation at lower temperatures as demonstrated with an 18.5 at. % sample. The lower curve Mössbauer temperature is 110 K, while the upper returns a θ_M of 128 K.

uncover significant evidence of precipitation until higher temperatures, along with longer anneal times below the precipitation limit, were used.

E. Complete characterization of large precipitates

The precipitation-dissolution reaction in the tin-lead system has been examined earlier using Mössbauer spectroscopy by Arriola and Cranshaw.[7] However, there are several important factors not taken into account in their work. Their data analysis was performed using Lorentzian fits to an assumed single line. While this is an accurate method of determining the center shift of one line, the very assumption that the resonance is a single line is flawed. Depending on the temperature at which the data point was taken there could be as many as three components superimposed upon each other, leading to a poor fit and an average value for the area of the resonance. In addition, even if multiple lines were used, fitting to Lorentzians will return incorrect parameters and hence incorrect areas, except in the ideal thin ($t \ll 1$) absorber limit which certainly did not hold for their case. Finally, no mention is made of tin perhaps precipitating in the α phase, and this possibility, which the present data confirms experimentally, is not considered in their analysis.

Therefore, each 80 K spectrum taken on the 18.5 at. % sample was first fit to a line-shape doublet represented by an analytic representation of the transmission integral. The position of each component in the spectrum was fixed to known values, with one representing dilute tin in lead and the other representing β-Sn. The linewidth of the tin resonance was allowed to float to account for the small unresolved splitting. This yielded a nearly satisfactory fit, with the returned χ^2 value of about 2. A further improvement was made by letting the linewidth of the solution line float, representing the likely possibility of very small precipitates (dimers and trimers) smearing out the dilute resonance.

A completely satisfactory fit to the data was found by allowing for the possibility of the tin precipitating out of the lattice into the α phase, known to have an isomer shift of 2.1 mm/s relative to a $CaSnO_3$ source.[15] Performing such a fit to the 18.5 at. % sample, when it was in a highly precipitated state ($\chi^2 = 28.4$ when fit to a single line), yielded an excellent fit, as shown in Fig. 5. The results of this fit yielded a χ^2 of 1.16, characteristic of a good fit to experimental data. Noting the relative intensities of the lines, it appears that the majority of the precipitate is in the β phase. The isomer shift of the α line was allowed to float, and returned a value of 2.02 mm/s. The residuals from this fit are presented in Fig. 6, and it can be seen that a good fit was indeed obtained. This is an exciting result, for we were not able to find any record in the literature of a Mössbauer experiment observing the α phase of tin in a precipitate. Furthermore, the α phase formed without the usual long incubation period required when grown from pure tin metal.

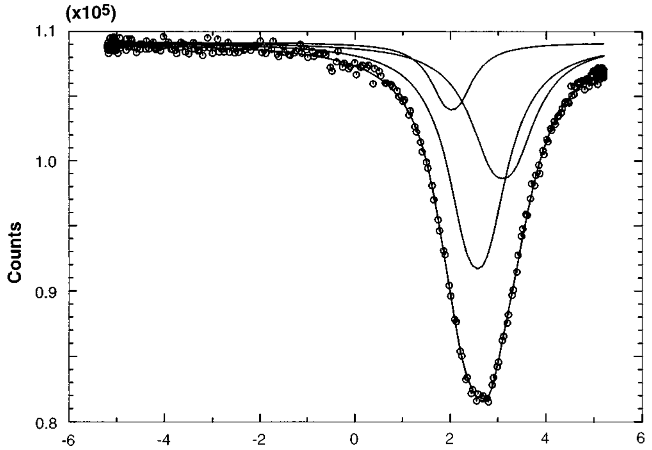

FIG. 5. The 18.5 at. % sample in a highly precipitated state. The fit was performed using three components as shown, corresponding to the α (III) and β (II) phases, and to tin in solution (I).

With the complete characterization of the Mössbauer data, the high-temperature properties could be examined. The experiment was performed by allowing the sample to anneal for 16–18 h and then rapidly quenching it to 80 K, where the spectrum was run. Figure 7 contains the Mössbauer thicknesses of each component of the spectrum as a function of anneal temperature. In the figure, the crosses are the α site, the triangles are the solution site, the circles are the β site,

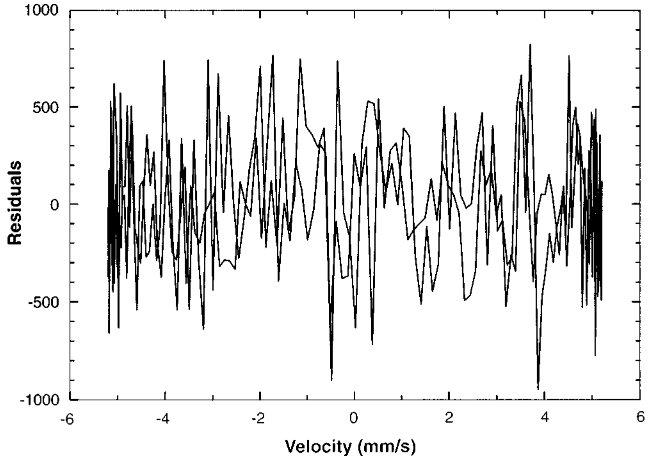

FIG. 6. Residuals from the fit performed on data taken with the 18.5 at. % sample while it was in a highly precipitated state.

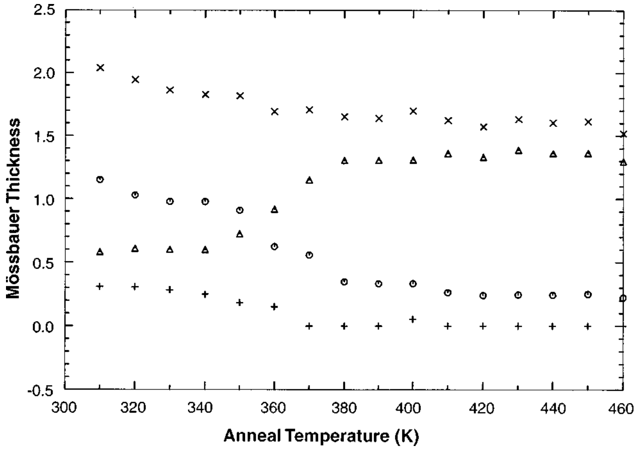

FIG. 7. Mössbauer thicknesses of each resonance as a function of anneal temperature. The crosses are the α site, the triangles are the solution site, the circles are the β site, and the x's are the sum. The ME data were all taken at 80 K and the error bars are not shown but reflect the general scatter in the data.

and the x's are the sum. As can be seen, the Mössbauer thickness of the solution site starts small and becomes much larger at the transition temperature of 360 K, while the thickness numbers of the precipitate sites do the opposite. The curve represented by the x's in the plot is the sum of the contribution to the resonance from each site. As would be expected, it stays relatively constant, with a slight decrease after the transition. The decrease is due to there now being relatively more tin in solution with the lower Debye temperature for this configuration. The small size of the decrease is because ^{119}Sn has a large recoilless fraction (near unity) at low temperatures (80 K) and is not very sensitive to differences in the Debye temperatures of the three components observed. We then take $360(+15/-5)$ K to be the dissolution temperature for an alloy of this composition, even though the 10 min quench time may require revising this number to a higher value when more rapid quenches can be carried out.

According to the lead-tin binary phase diagram as presented in Ref. 16, an 18.5 at. % sample should dissolve at a higher temperature. Thus, the dissolution curve may require a revision downward. The microscopic Mössbauer technique is more sensitive to the onset of dissolution than other techniques, and hence would show large scale changes in the pertinent parameters relatively early in the reaction. So this method could be quite useful in the study and possible correction of established phase diagrams.

Because our technique requires quenching our sample to 80 K, the high-temperature state frozen at 80 K may be lower than that where the anneal temperature was carried out. This systematic error could shift the data in Fig. 7 downward slightly and may explain some of the discrepancy between our observed dissolution temperature of 360 K and the higher value given in handbook phase diagrams. By using a redesigned apparatus, this discrepancy could be reduced or eliminated.

VI. CONCLUSION

^{119}Sn Mössbauer data has been taken on a variety of lead-tin alloys, ranging from the quite dilute (1.3 at. %) up to a tin concentrations of 18.5 at. %. Dilute samples were found to return an experimental Mössbauer temperature θ_M of 104 K, in general agreement with previously published values for dispersed tin in lead.[11] Furthermore, the dispersed state could be identified by the value of the isomer shift (3.00 mm/s), also in agreement with values reported in the literature. Finally, the dispersed state data could be easily fit to a single Mössbauer resonance, and no samples examined exhibited any behavior other than the typically expected Lamb-Mössbauer behavior, in direct contrast to the SSYBZ experiment reported elsewhere.[8,12]

In contrast to the dilute state, the presence of precipitates can be easily identified by their signature as found in the residual plots to single-line fits. Moreover, the returned value of the isomer shift is close to that of β-Sn. The Mössbauer signal depending on the relative size of the precipitates was also investigated, and it was found that in the first stages of precipitation the measured Mössbauer temperature was almost the same as in the dilute state. Therefore, small precipitates must couple to the lattice in a manner similar to that of isolated impurities. The larger precipitates gave values of θ_M much closer to that of bulk β tin, 140 K, indicating that they must be large enough to reflect some of the properties of the pure metal as seen in a Mössbauer experiment. Indeed, they could be easily located visually with the aid of a scanning electron microscope with a magnification as low as 5000X.

The actual precipitation-dissolution reaction was tracked with the aid of a cryostat capable of heating to the point of dissolution, 450 K, and then quickly cooling to a temperature where high-resolution Mössbauer spectra could be taken, 80 K. By following such parameters as the isomer shift and the relative intensities of signal coming from the solute site and the precipitate site(s), the dissolution was clearly observed in an 18.5 at. % doped tin in lead sample at 360 K. The sample was then quickly cooled to a lower temperature such that the supersaturated dispersed state would remain, and the then observed characteristic temperature matched that of the dilute state. Raising the sample temperature resulted in enough diffusive rearrangement that the large precipitates again formed, yielding an observed θ_M very close to that of the previously measured large precipitate state.

It is an exciting result that dispersed tin was found to precipitate in lead upon cooling directly into the α phase without the usual long incubation periods.[4] Furthermore, no references could be found in the literature pertaining to the observation of tin in both phases using Mössbauer spectroscopy. This experiment was in fact an excellent demonstration of the technique of fitting multiple single-line resonances to an analytic representation of the exact line shape for single-line spectra.

The method of fitting multiple resonances was also used to examine the high-temperature dissolution of tin into lead and to track the reaction as a function of anneal temperature. Each component in the spectrum was tracked and all showed that tin dissolves into a lead matrix at a temperature near 360 K, further indicating that the tin-lead binary phase diagram may need a slight modification, although a more rapid quenching apparatus would be needed to establish this claim.

In summary, Mössbauer spectroscopy can be a useful tool in the study of precipitation reactions and phase diagrams. The signature of small precipitates is indeed interesting, for they are clearly visible as isomer shifts in single-line curve-fits, but do not show up noticeably in recoilless fraction measurements of Mössbauer temperature. In direct contrast, larger precipitates do change the observed θ_M and approach the values found for the bulk form as the size of the precipitates increase. In the future, it would be desirable to perform more detailed measurements of the precipitation-dissolution reaction using Mössbauer spectroscopy. Specifically, data taken at closer temperature intervals with very rapid quench times would be beneficial in making precise determinations of phase diagrams. In this manner, the reaction could be tracked in quite close detail.

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