

Anomalous Local Hopping of Sn Impurities in Lead

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(Received 13 March 1989)

The Mössbauer spectral intensity of ^{119}Sn impurities in Pb with concentrations of 5%, 2%, 1%, and $\frac{1}{2}\%$ is measured as a function of temperature. A single narrow line is observed which slightly narrows as the temperature increases. Above a temperature $T_c \ll T_m$, the bulk melting temperature, the Mössbauer integrated intensity drops precipitously from a Debye-Waller behavior. Analysis of the results shows that a small region around each Sn atom is in a state of relatively large entropy, suggesting a local behavior more similar to a liquid than a solid.

PACS numbers: 66.30.Jt, 64.70.Dv, 76.80.+y

X-ray absorption fine-structure (XAFS) measurements on Hg impurities in Pb give evidence for a local behavior which was interpreted as a premelting phenomenon.¹ The vibrational amplitudes of the Hg atoms tended to saturate for temperatures well below bulk melting temperature T_m and the local diffusion increased to the liquid value just below T_m , which is about 5 orders of magnitude larger than the bulk solid diffusion rate. It was speculated that this behavior is a general one and that the sites about those impurities which lower the bulk melting temperature T_m act as initiation sites for three-dimensional (3D) melting. Even in pure materials, it was suggested that vacancies will act as initiation sites for 3D melting. In a rough picture, a small region around the impurities and vacancies near, but below, T_m will be melted.

To verify the XAFS results by an independent method and to study another impurity, we present here Mössbauer measurements made on Sn impurities in Pb. The results indicate a rapid drop of the Mössbauer spectral intensity I (the integrated resonance absorption intensity) below a Debye-Waller behavior at a critical temperature $T_c \approx 150$ K ($T_m = 600$ K) for concentrations of Sn of 1% and $\frac{1}{2}\%$. At these concentrations and temperatures, the Sn atoms act as isolated impurities in the Pb matrix.² These results again indicate an anomalous local behavior of an impurity in Pb, in this case Sn, which is consistent with the anomalous behavior of Hg impurities in Pb. In both cases, as we discuss, the local behavior more closely resembles that of a liquid than a solid, in spite of the fact that the alloy is clearly a solid in its bulk state.

The samples for the Mössbauer measurements were prepared from 99.999% pure Pb and from Sn that was enriched to 84% of the isotope 119. The Pb and Sn of the appropriate weights were placed in a glass tube, evacuated and sealed. The metals were melted and mechanically mixed by shaking and subsequently kept liquid for 24 h to obtain a homogenized liquid. The sample was air

quenched after removal from the furnace. After removal from the tube, the ingot was rolled into a foil 0.0025 cm thick, which was covered with a 1000-Å Al film to inhibit oxidation. Four concentrations of 5, 2, 1, and 0.5 at. % of Sn were prepared in this manner. The Sn concentration of the foils were confirmed by Auger depth analysis. According to the phase diagram,³ Sn dissolves into the Pb matrix for concentrations below about 3 at. % at room temperature, with a trend of lower concentration as the temperature decreases.

The Mössbauer measurements were performed with the Pb:Sn alloy as the fixed absorber which was cooled by a system that controlled the temperature to within 0.1 K by flowing liquid He or nitrogen. A ^{119}Sn γ source (24 keV) in a BaSnO₃ matrix was used in a constant acceleration drive.

The experiment yields a Mössbauer single-line absorption pattern analyzed as a Lorentzian line shape to obtain its position δ_{expt} , width, and spectral intensity I . Figure 1 presents the temperature dependence of $\ln I$ for the various alloys. The temperature dependence of the linewidth is shown in the inset. The spectral intensities I of the 1% and 2% samples were normalized relative to the I (78 K) of the 5% sample. If the Sn impurities are only vibrating, one expects that $\ln I = -2W$ (the Debye-Waller factor). Deviations from a linear T behavior of W are expected at both low and high temperatures. The low-temperature deviation is from quantum effects, while the high-temperature deviation is from anharmonicity. However, the results in Fig. 1 are striking because of the very rapid decrease of $\ln I$ at the upper temperatures, much too rapid to be expected from anharmonicity, especially for the lower concentrations.^{4,5} On the other hand, the linewidth remains small and even narrows slightly as the temperature increases. The interpretation of the higher concentration samples is complicated by the fact that they are not homogeneous. The 5% Sn is partially precipitated out and partially dissolved. We are interested in the case of isolated Sn impurities and, in

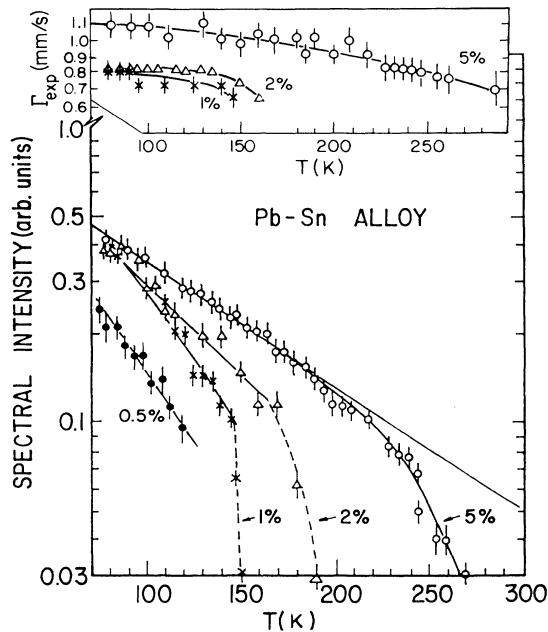


FIG. 1. Mössbauer spectral intensity vs T of ^{119}Sn atoms at the indicated atomic percentage concentration in Pb. The various curves, except the 0.5% one, are normalized to the value of 5% at 78 K. The 0.5% curve is displaced downward for clarity. The thick solid and dashed curves are drawn through the experimental points as a guide for the eye. A straight line is drawn through the lower-temperature portion of the 5% data points to indicate the deviation that occurs at higher temperatures. Inset: Corresponding Mössbauer linewidths as a function of T .

this limit, the Mössbauer behavior should be independent of concentration. This independence is found for the 1% and $\frac{1}{2}$ % samples. Interestingly, the 2% sample does not show this independence, even though the phase diagram indicates that all the Sn is dissolved.

There are two features that behave differently as a function of concentration. One is the slope in the linear T range and the other is the temperature T_c where $\ln I$ starts to rapidly drop below the Debye-Waller behavior. There are several approximate ways to estimate the slope for an impurity. In the classical limit of the harmonic Debye approximation,⁶ the slope is

$$s = \frac{-3\hbar^2 k^2}{Mk_B\Theta_{\text{eff}}^2},$$

where the Debye temperature is Θ_D , the mass of the impurity is M_i , that of all the other atoms is M , k_B is the Boltzmann constant, and

$$\Theta_{\text{eff}}^2 = \Theta_D^2 \frac{M}{M_i}.$$

A highly localized impurity vibration mode can be ap-

proximated by the Einstein approximation giving

$$s = \frac{-\hbar^2 k^2}{M_i k_B \Theta_E^2},$$

where Θ_E is the Einstein temperature. The general expression⁷ is different from these two cases, but in any case, the slope is inversely proportional to the square of some characteristic temperature Θ associated with the impurity.

As noted from Fig. 1, as the concentration decreases down to 1%, both Θ and T_c decrease. Below 1%, Θ becomes constant. The signal was too weak to observe T_c for the $\frac{1}{2}$ % sample, but since its Θ is the same as the 1% sample, it is reasonable to assume that both concentrations represent isolated impurities and thus will have the same T_c . It is important to notice in the inset of Fig. 1 that the linewidth remains constant and perhaps even decreases slightly during the rapid drop of I .

In interpreting the results in Fig. 1, we limit ourselves to the 1% data since only they are representative of a homogeneous environment about the impurities, namely, isolated Sn atoms in the Pb matrix. The decrease at $T_c \approx 147$ K is much too rapid to be explained by anharmonicities in the vibrations of the Sn impurities. For comparison, the anharmonicity in pure Sn is a much more gradual effect.⁵ To explain this rapid decrease it is necessary to assume that the Sn diffuses from its low-temperature position. However, since Sn is not an anomalously fast diffuser in Pb and the bulk diffusion coefficient⁸ is negligibly small at this temperature, the diffusion must be localized; namely, it must involve a finite number of states in the immediate vicinity of the low-temperature position of the Sn. Besides, bulk diffusion broadens⁹ the Mössbauer line with no narrow line remaining, contrary to the measurement. The observed line narrowing is small and if real may be caused by effects secondary to the atomic motion. The main point is that we detect no line broadening.

We are led to consider whether the model suggested by the XAFS results is also consistent with the Mössbauer results. The simplest model of this kind is to assume that the Sn and its surrounding Pb atoms can be in two types of states. The first is the low-temperature state where the Sn is vibrating about its lattice site, and the second is an excited state where the Sn has hopped away from its lattice site, with the surrounding Pb atoms displaced to accommodate this motion. For simplicity, we approximate the spatial distribution of the Sn in the second state by a Gaussian rms width σ_2 . The vibration of the Sn atom in the low-temperature state is described by a Gaussian distribution function of rms width σ_1 . In this case, the Mössbauer intensity can be written, using the Fourier transform formalism of the self-correlation function as introduced by Singwi and Sjölander,⁹ as $I = \int W d\omega$, where W is a function of the frequency ω and wave number k of the γ ray and is expressed in the

following form:

$$W(k, \omega) = Pe^{-k^2\sigma_1^2}P\mathcal{L}(\Gamma, \omega) + (1-P)\mathcal{L}(\Gamma+\Delta, \omega) + 2P(1-P)e^{-(k^2/2)(\sigma_1^2+\sigma_2^2)}[\mathcal{L}(\Gamma, \omega) - \mathcal{L}(\Gamma+\Delta, \omega)] \\ + (1-P)e^{-k^2\sigma_2^2}[(1-P)\mathcal{L}(\Gamma, \omega) + P\mathcal{L}(\Gamma+\Delta, \omega)]. \quad (1)$$

Here P is the probability of finding the Sn in the low-temperature state; $\Gamma/2$ is the Mössbauer natural linewidth; $(\Delta/\hbar)^{-1}$ is the relaxation time of the distribution function to its equilibrium value, and the Lorentzian:

$$\mathcal{L}(\Gamma, \omega) = \frac{2\Gamma/\hbar}{(\omega - \omega_0)^2 + (\Gamma/\hbar)^2}.$$

In the Lorentzian $\hbar\omega_0$ is the resonant energy of the Mössbauer line and Γ appears instead of $\Gamma/2$ since the experimental linewidth is a convolution of those of the emitter and absorber.

In principle, there are three ways to account for the decrease in the peak intensity with temperature: One is to assume that Δ changes continuously from a value small compared to the natural linewidth $\Gamma/2$ at low temperatures to a value which is large compared to it above T_c . Notice that in this case the integrated intensity does not change with temperature. As the temperature increases part of the line broadens continuously, keeping its integrated intensity constant. Bulk diffusion is of this type.⁹ This result is inconsistent with the experimental results. We observe only one Lorentzian line and as shown in Fig. 1, its width decreases slightly with temperature. To further verify this point we calculated the integrated intensity included between the Mössbauer spectrum and a flat base line. The base line is obtained by interpolating the flat part of the spectrum far away from the line. The range of integration was more than 10 times the FWHM of the observed line. The temperature dependence of the integrated intensity calculated in this way is identical to the results in Fig. 1, indicating that no other line is hiding in the spectrum.

In the remaining two cases, we assume that $k^2\sigma_2^2 \gg 1$. They are the following: (a) $\Delta \ll \Gamma$. In this case,

$$W(k, \omega) = [Pe^{-k^2\sigma_1^2}]\mathcal{L}(\omega, \Gamma); \quad (2)$$

(b) $\Delta \gg \Gamma$. In this case,

$$W(k, \omega) = [P^2e^{-k^2\sigma_1^2}]\mathcal{L}(\omega, \Gamma). \quad (3)$$

Thus, as the temperature increases, the probability P decreases and the integrated line intensity decreases without broadening.

The probability to find the Sn in the various states is determined by the Boltzmann distribution

$$P/(1-P) = N^{-1}\exp(E/k_B T). \quad (4)$$

Here E is the energy difference between the two types of states and N is the number of states of type 2. It is easily seen that if N is equal to N_s , the number of off-center positions of the Sn atom, the temperature dependence

expressed in Eq. (4) is completely inadequate to account for the rapid decrease of the intensity with temperature. We therefore have to assume that the states of type 2 may differ from each other not only in the positions of the Sn atom but also in the positions of the Pb atoms surrounding it. We therefore assume that at and above the critical temperature, a number L of Pb atoms within a small bubble around the Sn may change their positions. The number of states N in this case is of the order of $N_s 2^L$. $k_B \ln(N/N_s) = S$ has the meaning of a local entropy. Substituting this entropy into Eq. (4) yields

$$P/(1-P) = N_s^{-1} \exp[(E - TS)/k_B T]. \quad (5)$$

Namely, in calculating the probabilities, we should consider not the energies but the free energies of the various Sn states. Using Eq. (5) we can reproduce the experimental observation quantitatively with the following parameters. Case (a) $\Delta \ll \Gamma$: $E = 500$ meV, $S = 3.1$ meV/K, $L \approx 55$. Case (b) $\Delta \gg \Gamma$: $E = 450$ meV, $S = 2.7$ meV/K, and $L \approx 45$. The experimental results cannot distinguish between these two cases.

The number of atoms in the bubble estimated from this analysis agrees well with the fact that the Sn behaves as an isolated atom only below concentrations of 2%, namely, when the Sn is surrounded by more than 50 Pb atoms. We therefore estimate that the bubble size is about 8 Å in diameter.

The usual definition of a liquid is based on the loss of long-range order that is present in the solid. In our case, we are discussing a region so small that this definition cannot be employed, introducing the question of how one can distinguish a liquidlike region surrounding the impurity. There are at least two ways to do so. One is the local hopping constant. The second is the entropy density, which is significantly higher in the liquid. The Mössbauer results indicate the surprising result that the Sn impurity is surrounded by a bubble of Pb atoms which are in a state characterized by a large amount of entropy. In this sense this bubble is liquidlike. This bubble has this large entropy content at a temperature much lower than the melting temperature T_c .

The results reported here are quite unexpected and the question arises whether any other published results can help understand or confirm these results. We list some of these here. Recent high-resolution electron microscope observations¹⁰ and calculations¹¹ have suggested that for small enough particles a quasimolten phase can exist where the particles are continuously fluctuating between different structures at temperatures well below T_m . As the particles get smaller, the temperatures where

these molten features occur get lower. An isolated impurity is, of course, the extreme limit of a small particle. The results in Fig. 1 show qualitatively the same trend of a lowering of T_c as the particle size gets smaller.

Solid-solid interfaces have been found to be liquid below the bulk melting temperature T_m . There is much evidence of melting at grain boundaries below T_m .¹²⁻¹⁴ Temperature dependence of the resistance of pure Pb gives evidence of a defect consisting of a vacancy surrounded by a melted bubble as T_c was approached from below.¹⁵ In some sense, a vacancy can be perceived as an impurity in the perfect Pb matrix. Quasielastic neutron scattering experiments performed on the superionic conductor AgI also show evidence of two diffusion times, one being a fast localized motion, the other being a slow long-range diffusion.¹⁶

Our results may be a mechanism for the atomic tunneling phenomena¹⁷ which are observed at low temperature in both glassy and crystalline solids. The effects are not expected in perfect crystals, but real crystals show this glassy behavior, though at a substantially reduced magnitude.¹⁸ The magnitude increases as more defects are introduced in the crystals. Diffusion of defects at low temperatures have been suggested as an explanation of time variations in the magnetic field dependence of the conductance in the quantum limit¹⁹ and of low-temperature $1/f$ noise.^{19,20}

Finally, an unusual local hopping phenomena was found²¹ for self-interstitials trapped at Co in Al. The Al interstitials were produced by low-temperature irradiation with high-energy electrons. Mössbauer spectroscopy on the ⁵⁷Co impurities indicated a rapid decrease in the recoilless fraction by more than a factor of 4 in the temperature interval between 13 and 20 K. This unusual behavior was attributed to the Co atom being itself in an interstitial site as it formed a dumbbell defect with an Al interstitial across the face of the unit cell cube. It was postulated that the Co interstitial hopped between the six equivalent sites corresponding to forming dumbbell defects across each face of the unit itself. This hopping was thermally activated in a temperature interval 13-20 K to cause the rapid drop in the recoilless fraction. Such a model cannot fit our situation as our samples are well annealed and we do not expect any significant number of self-interstitials to exist. The phase diagram for Pb Sn as verified by diffraction indicates that Sn is a substitutional impurity, not an interstitial one.

In summary, Mössbauer measurements on Sn impurities in a Pb matrix show that a small bubble of Pb atoms around the Sn impurity is in a state characterized by a relatively large entropy content, suggesting that this bubble is liquidlike. This bubble is confined to a region of less than 8 Å in diameter. The results are consistent with previous XAFS measurements on Hg impurities in Pb and with a model of a highly deformable bubble sur-

rounding the impurity.

One of us (E.A.S.) is happy to acknowledge stimulating conversations with John W. Cahn. The Research of E.A.S. and Z.Z. was supported by the U.S. DOE under Contract No. DE-A505-80-ER10742. The research of H.S., R.B., and Y.Y. was supported by the U.S.-Israel Binational Science Foundation.

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