Lattice dynamics of ^{119}Sn impurities in Pd†

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The temperature dependence of the Mössbauer effect has been measured at ^{119}Sn nuclei in $Pd_{0.99}Sn_{0.01}$. The thermal shift and recoil-free fraction have been interpreted using the neutron-determined phonon density of states and Mannheim's impurity model. The forces between the Sn atom and the Pd host are found to be increased relative to the Pd-Pd coupling.

The dynamics of impurity atoms in crystal lattices have received considerable experimental and theoretical attention in recent years. This paper presents the results of a Mössbauer investigation of the lattice properties of ^{119}Sn atoms in $Pd_{0.99}Sn_{0.01}$. We make use of the theoretical results of Mannheim and co-workers,[1] who have treated the lattice dynamics of a substitutional impurity in a cubic lattice. The assumptions employed are that the impurity-lattice interaction is harmonic, that only the nearest-neighbor force constants to the impurity differ from those of the host, and that the impurities are isolated from each other.

In a recent treatment by Cohen *et al.*,[2] Mannheim's impurity theory[1] has been applied to Mössbauer data in dilute alloys; the analysis utilizes neutron-determined phonon density of states and takes weak anharmonicity into account. The ratio of the near-neighbor impurity-to-host A' to host-to-host A force constants and differences in anharmonicity between the dilute alloy and the host lattice are determined. (Note: an extensive literature exists on host-impurity interactions. The references given in Ref. 2 give the main body of recent Mössbauer work.)

Our Mössbauer measurements utilized a system that precisely fixes the source and absorber temperatures.[3] The velocity drive, calibration-source, calibration-absorber, and Mössbauer source are installed in a chamber thermally controlled to 273.56 ± 0.03 K. The Pd+Sn absorber is held in a variable-temperature helium Dewar and is temperature controlled to ± 0.05 K. The ^{119}Sn source used was $BaSnO_3$ (full width at half maximum $\Gamma = 0.46$ mm/sec). The experiments were performed on Pd+Sn alloys formed by melting 99.9999%-pure Pd (<1 ppm Fe) and 99.999%-pure tin in a levitation furnace; the highly agitated melts were helium gas quenched in order to solidify the alloy without contact with any solid surface. The ingots were precision rolled to specified thickness, taking special precautions to avoid ferrous contamination, and then stress relief annealed.

Figure 1 is a typical ^{119}Sn Mössbauer absorption spectrum obtained in our $Pd_{0.99}Sn_{0.01}$ experiments. The single-line absorption is analyzed with a Lorentzian line shape to obtain the position δ_{exp}, width, and intensity of the line. In a harmonic model the area A or integrated resonance absorption intensity is related to the Debye-Waller factor, i.e., $-\ln A \sim -\ln f = K^2\langle X^2\rangle$, where f is the recoil-free fraction, K is the wave number of the 23.88-keV γ ray, and $\langle X^2\rangle$ is the mean-squared displacement of the absorbing atom. The position δ_{exp} is related to the mean-squared velocity $\langle v^2\rangle$ and the isomer shift δ_{IS}, i.e., $\delta_{exp} = \delta_{IS} + \langle v^2\rangle/2c$, where c is the velocity of light.

Following Mannheim, we write the mean-squared displacement and velocity of the impurity of mass

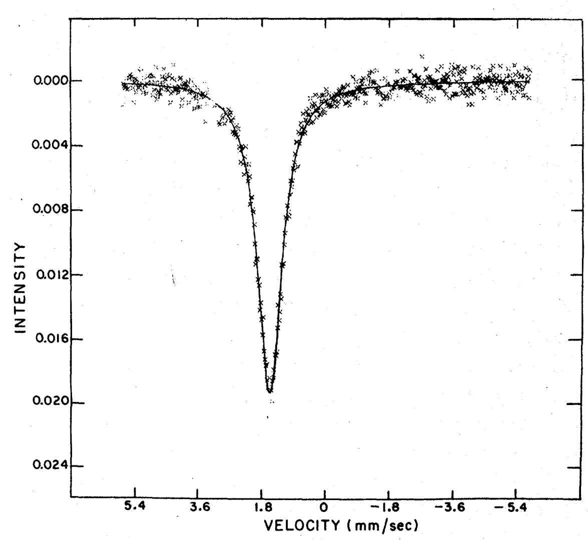

FIG. 1. Mössbauer absorption spectrum for $Pd_{0.99}Sn_{0.01}$ foil (22.9 μm thick) at 77.3 K.

M' in the host of mass M and impurity phonon spectral density $G'(\omega)$ as

$$\langle X^2 \rangle = \frac{\hbar}{2M'} \int_0^\infty G'(\omega) \coth\left(\frac{\omega}{2T}\right) \omega^{-1} d\omega , \quad (1)$$

$$\langle v^2 \rangle = \frac{\hbar}{2M'} \int_0^\infty G'(\omega) \coth\left(\frac{\omega}{2T}\right) \omega \, d\omega , \quad (2)$$

and

$$G'(\omega) = (M/M')G(\omega)\{[1+\rho(\omega)S(\omega)]^2 + [\tfrac{1}{2}\pi\omega G(\omega)\rho(\omega)]^2\}^{-1} + \delta(\omega-\omega_L)(M/M')\{\rho^2(\omega)T(\omega) + (M/M') - [1+\rho(\omega)]^2\}^{-1} , \quad (3)$$

where

$$\rho(\omega) = M/M' - 1 + \omega^2(M/A)(1 - A/A') , \quad (4)$$

$$S(\omega) = P \int \omega'^2(\omega'^2 - \omega^2)^{-1} G(\omega') d\omega', \quad (5)$$

and

$$T(\omega) = \omega^4 \int (\omega'^2 - \omega^2)^{-2} G(\omega') d\omega' . \quad (6)$$

The second term in Eq. (3), involving the Dirac δ function at the localized mode frequency ω_L, contributes only if a localized mode exists with ω_L greater than the maximum frequency of the host spectral density $G(\omega)$. The condition necessary for a local mode to exist is given by

$$1 + \rho(\omega)S(\omega) = 0 . \quad (7)$$

Thus, $\langle X^2 \rangle$ and $\langle v^2 \rangle$ can be calculated for the ^{119}Sn impurity in Pd with only one adjustable parameter A/A'. We have made that calculation based on the Miller and Brockhouse[4] $G(\omega)$ of Pd determined at 120 and 296 K. For $A/A' = 1.0$, the effect of the heavier Sn mass is to soften $G'(\omega)$ relative to $G(\omega)$. This is exactly opposite to the result obtained by fitting the experimental Mössbauer results for the ^{119}Sn thermal shift $\delta_{th} \sim \langle v^2 \rangle$ to a Debye model, i.e., using a Debye distribution $G'(\omega) \sim \omega^2$ for $0 \le \omega \le \theta_\delta$ in Eq. (2). That is, the temperature dependence of the Mössbauer shift yields θ_δ greater than that expected from the host Pd phonon spectral density. Thus, we have examined solutions of Eq. (3) with $A/A' < 1.0$, i.e., for stronger Sn-Pd nearest-neighbor force constants. In Fig. 2 we illustrate $G(\omega)$ and $G'(\omega)$ (normalized to unity) at $T = 120$ K for $A/A' = 1.0$, 0.9, and 0.6. In Figs. 3 and 4, we compare the experimental values of $K^2 \langle X^2 \rangle$ and δ_{exp} to the calculated values from Eqs. (1) and (2) for values of $A/A' = 1.0$, 0.7, 0.6, and 0.5. Here $\delta_{calc} = \langle v^2 \rangle / 2c$.[3] We note that the calculated shift δ_{calc} is unchanged if we use the 296-K spectra; however, there is a difference in the calculated $K^2 \langle X^2 \rangle$ for $G(\omega)$ at 120 K and $G(\omega)$ at 296 K as illustrated for $A/A' = 0.6$ in Fig. 3. We find that within the accuracy of our data we can fit $K^2 \langle X^2 \rangle$ and δ vs T with $A/A' = 0.6 \pm 0.1$, and with negligible differences in anharmonic contribution between pure Pd and $Pd_{0.99}Sn_{0.01}$. Cohen *et al.*[2] also find negligible differences in anharmonic contribution for Fe in Pd, but find that $A/A' = 1.70$. Prince *et al.*[5] find that the ratio of the host-host to impurity-host force constant is less than one for Au impurities in both Cu and Ag matrices.

It is interesting to note the trends in the spectra in Fig. 2. The sharp high-energy peak in $G(\omega)$ for Pd is due to the relatively dispersionless longitudinal-acoustic modes at large wave vector and $\omega \simeq 300$ K. There is an additional maximum in the spectrum because the transverse acoustic modes are also relatively dispersionless near $\omega = 195$ K. The effect of the heavier mass Sn impurity with $A/A' = 1$ is to soften $G'(\omega)$ relative to $G(\omega)$ in the long-wavelength (low-energy) region. However, for shorter wavelengths (higher energy) the Sn motion is relatively uncoupled from the Pd; the high-energy peak in $G(\omega)$ is highly attenuated in $G'(\omega)$. As we stiffen the Sn-Pd nearest-neighbor force constant, $A/A' = 0.9$, the long-wavelength (low-energy) modes in $G'(\omega)$ are hardened relative

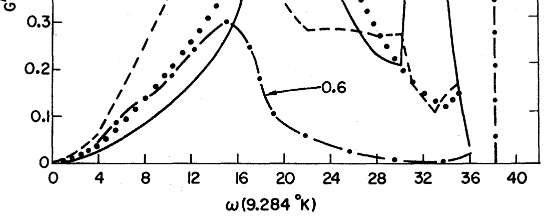

FIG. 2. $G(\omega)$ at 120 K for Pd[4]. $G'(\omega)$ for $A/A' = 1.0$, 0.9, and 0.6. Local mode for $A/A' = 0.6$, shown by arrow, has $\frac{2}{3}$ weight of $G'(\omega)$. All distributions are normalized to 10.0.

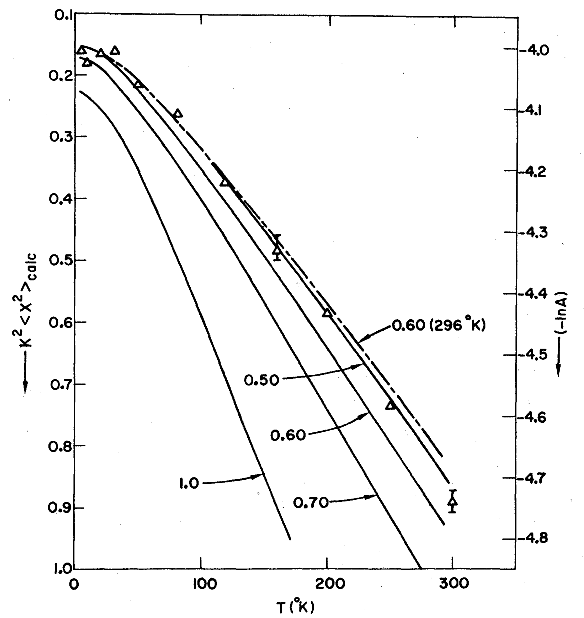

FIG. 3. $K^2\langle X^2\rangle_{\text{calc}}$ for $A/A'=1.0$, 0.7, 0.6, and 0.5 for $G(\omega)$ at 120 K and $A/A'=0.6$ for $G(\omega)$ at 296 K. Experimental data for $Pd_{0.99}Sn_{0.01}$ indicated by Δ. The data are normalized to $f=0.41$ at 300 K (Ref. 6); $\langle X^2\rangle_0^{1/2}$ is then 0.036 Å. A fit of the Mössbauer data to a Debye model yields $\theta_f = 242 \pm 4$ K.

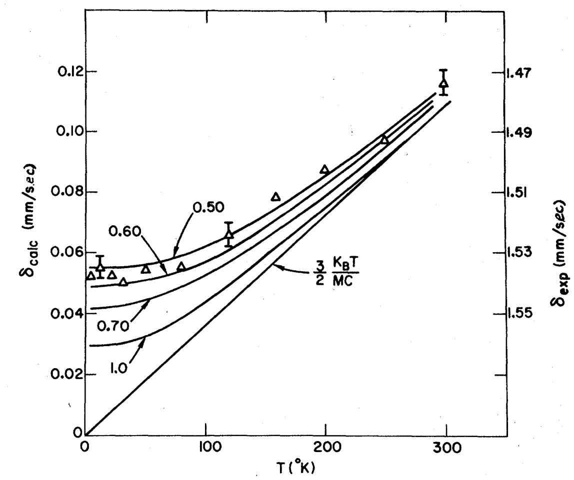

FIG. 4. δ vs T is calculated for $A/A'=1.0$, 0.70, 0.60, and 0.50 for $G(\omega)$ at 120 K. Experimental data for $Pd_{0.99}Sn_{0.01}$ are given by Δ (with scale at right). A fit of the Mössbauer data to a Debye model yields $\theta_\delta = 383 \pm 15$ K and $\langle v^2\rangle_0^{1/2} = (1.7 \pm 0.1)\times 10^4$ cm/sec. The shift at 296 K is 1.473 ± 0.005 mm/sec relative to the $BaSnO_3$ source at 296 K is in good agreement with the results of previous workers (Ref. 7).

to $A/A'=1.0$, but the high-energy modes of the Sn are still attenuated relative to the host. Finally, for $A/A' \lesssim 0.7$ a local mode splits out of the continuum and modes of $G(\omega)$ with $\omega \gtrsim 200$ K are uncoupled from the Sn.

We note that for $A/A'=0.6$ about $\frac{2}{3}$ of the weight of $G'(\omega)$ is in the local mode at energy $\omega_L = 356$ K. Since $\langle v^2\rangle$ is weighted by the high-energy modes, it is determined by ω_L and is slightly harder than what would have been determined by the longitudinal peak in $G(\omega)$ of Pd. On the other hand, $\langle X^2\rangle$ is weighted more by the low-energy (long-wavelength) modes and is quite similar to that calculated from $G(\omega)$ of Pd.

There is some advantage in using Mössbauer data over a broad temperature range even with relative f measurements because the accuracy of absolute f determinations is often less than that which can be obtained in measurements of relative f as a function of temperature. Moreover, $\ln f \sim \langle X^2\rangle$ is proportional to the thermal average of $\langle \omega^{-1}\rangle$ and is most sensitive to the low-frequency part of $G(\omega)$. We note that in the neutron measurements the low-frequency part of $G(\omega)$ has the greatest experimental uncertainty, and the use of elastic constant measurements is often a more precise way of determining the low-frequency part of $G(\omega)$.

In summary, we find a large increase in the Pd-Sn force constant relative to the Pd-Pd nearest-neighbor force constant and a negligible difference in anharmonicity between Pd and $Pd_{0.99}Sn_{0.01}$. Although Sn is slightly heavier than Pd, the increased Pd-Sn force constant leads to a local mode in the Sn vibrational motion, which contains a large fraction of the Sn spectral density.

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