UNAMBIGUOUS DETERMINATION OF FORCE CONSTANT CHANGE OF MÖSSBAUER ^{119}Sn IMPURITY NUCLEI IN PALLADIUM HOST

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Generally reported impurity-host force constant ratios are ambiguous as anharmonic effects are not accounted for. Using anharmonic theory for highly dilute Sn in Pd we find an impurity-host to host-host force constant ratio $A_H'(a_{\text{eff}})/A_H(a) = 1.69 \pm 0.03$.

1. Introduction

Various simplified impurity lattice models have been used in the literature to obtain effective host-impurity force constant ratios, A'/A from Mössbauer fraction and thermal shift measurements in highly dilute alloys. Recently Landuyt et al [1] measured the temperature dependence of the Mössbauer effect in ^{119}Sn nuclei in $Pd_{0.99}$ $Sn_{0.01}$. They used impurity theory [2, 3] and phonon frequency spectrum $G(\omega)$ [4] of Pd to analyse their experimental data. The forces between the Sn impurity and Pd host were reported to be stronger relative to the Pd—Pd coupling. On the other hand, similar Mössbauer measurements of Puri and Gupta [5] but analysed by using a Debye spectrum of Pd and Mannheim's theory [3] yield exactly opposite results. Further, Gloss and Shukla [6] have pointed out that Θ-T curves of Pd exhibit a trend to rise up further at higher temperatures indicating that lattice anharmonicity must account for an unambiguous determination of A'/A. Maradudin and Flinn [7] have shown that the anharmonic contribution to the mean squared displacement of an impurity is given as

$$\langle x^2 \rangle_T = \langle x^2 \rangle_T^H (1 + \varepsilon T), \tag{1}$$

where $\langle x^2 \rangle_T^H$ is assumed to correspond to the value as predicted by the harmonic theory. Mannheim's theory [2, 3] gives good agreement with the experimental data over a wide temperature range, if we make a fit involving both the force constant ratio A'/A as well as the anharmonicity parameter ε from Eq. (1).

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This is what LANDUYT et al [1] have done. However, force constant ratios A'/A so obtained remain ambiguous because ε, and also the co-fitted value A'/A, contains an unspecified admixture of various effects of temperature in the pure host, together with those of the impurity-host lattice interaction, as well as possible relaxation effects due to the introduction of the impurity. COHEN et al [8] have shown that for host systems where neutron data are available at different temperatures T_i, it is possible to obtain an unambiguously defined impurity-host force constant ratio.

2. Impurity dynamic response function $G'(\omega)$ and the inverse ratio A/A'

Following COHEN et al [8] let us denote a harmonic force constant by $A_H(a)$ and a "real" or "effective" force constant by $A_{\mathrm{eff}}(T)$. The definition of $A_H(a)$ in terms of the second derivative of the potential for a cubic lattice [2, 3] is

$$A_H(a) = A_{xx}(0, 0) = - \sum_{l \neq 0} A_{xx}(0, l), \tag{2}$$

where l stands for the lattice sites and a is the lattice constant at a given temperature T. Though the summation in Eq. (2) extends to nearest neighbours only, the parameter $A_{xx}(0,0)$ is unambiguously defined as a sum over all atoms in the crystal. As MANNHEIM has pointed out [3] the assumed proportionality between $A_H(a)$ and $\omega_{\max}^2$ in the theoretical expressions for $\langle x^2 \rangle_T$ and $\langle v^2 \rangle_T$ for the atom at the origin is strictly true if the interactions are limited to nearest neighbours: it must be modified, if more distant neighbours are included. The force constant $A_{xx}(0,0)$, however is uniquely defined for any lattice model, including nth-neighbour interactions, from which $G(\omega)$ has been obtained. Therefore, the actual value of $A_{xx}(0,0)$ for the host should be used in the theoretical expressions, rather than $1/2 M\omega_{\max}^2$ for the evaluation of the dynamic response function $G'(\omega)$ of the impurity [2, 3, 9]

$$\langle x^2 \rangle_T = \frac{\hbar}{2M'} \int_0^\infty \omega^{-1} \coth \left(\frac{\frac{1}{2} \hbar\omega}{k_B T} \right) G'(\omega) \, dw \tag{3a}$$

with

$$G'(\omega) = (M/M') \, G(\omega) \left\{ [1 + \varrho(\omega)S(\omega)]^2 + \right.$$

$$\left. + \left[\frac{1}{2} \pi\omega \, G(\omega) \, \varrho(\omega) \right]^2 \right\}^{-1} + \delta(\omega - \omega_L) \, (M/M') \times$$

$$\times \{ \varrho^2(\omega) \, T(\omega) + (M/M') - [1 + \varrho(\omega)]^2 \}^{-1}, \tag{3b}$$

where

$$\varrho(\omega) = M/M' - 1 + \omega^2 (M/A)(1 - A/A') , \tag{3c}$$

$$S(\omega) = P \int \omega'^2 (\omega'^2 - \omega^2)^{-1} G(\omega') \, d\omega', \tag{3d}$$

$$T(\omega) = \omega^4 (\omega'^2 - \omega^2)^{-2} G(\omega') \, d\omega' , \tag{3e}$$

and $\delta(\omega - \omega_L)$ is the Dirac δ function at the localised mode frequency ω_L, provided a localized mode exists. In Eq. (3c), $A = A_{xx} (0, 0)$ as defined by Eq. (2) and $A' = A'_{xx} (0, 0)$, the impurity-host force constant, is defined in a similar way, with the impurity located at the origin and the sum over l restricted to nearest neighbours.

Lattice expansion effects can be included in $A_H(a)$, and in $A_{\text{eff}}(T)$ we include any other harmonic effects. Following similar reasoning as for the mean-squared displacement [Eq. (1)], it is therefore physically appropriate to relate these effects to the force constants in the following manner:

$$A_{\text{eff}}(T) = A_H(a) (1 - \varepsilon_h T) , \tag{4a}$$

where ε_h now describes the combined anharmonic contributions to the force constants [Eq. (2)] in the host.

Similarly when the impurity is introduced into the lattice one may write

$$A'_{\text{eff}}(T) = A'_H(a_{\text{eff}}) (1 - \varepsilon_i T) . \tag{4b}$$

In this equation the primes denote the changed values of the force constant and ε_i stands for the anharmonic parameter in the presence fo the impurity. The inverse force constant ratio A/A' [Eq. (3c)] appearing in MANNHEIM's impurity theory [2, 3] is the ratio $A_{\text{eff}}(T)/A'_{\text{eff}}(T)$; therefore, we write

$$\frac{A_{\text{eff}}(T)}{A'_{\text{eff}}(T)} = \frac{A_H(a) (1 - \varepsilon_h T)}{A'_H (a_{\text{eff}}) (1 - \varepsilon_i T)} . \tag{5}$$

It is known [6] that typical anharmonicity parameters are of the order 10^{-4} K^{-1}, so that we can safely expand the denominator in Eq. (5) to get

$$\frac{A_{\text{eff}}(T)}{A'_{\text{eff}}(T)} = \frac{A_H(a)}{A'_H(a_{\text{eff}})} \left[1 + (\varepsilon_i - \varepsilon_h) T + 0 (\varepsilon_i \varepsilon_h) \right]. \tag{6}$$

3. Application to $Pd_{0.99} Sn_{0.01}$ system

In Fig. 1 we show values of $A_{\text{eff}}(T)/A'_{\text{eff}}(T)$ for $Pd_{0.99} Sn_{0.01}$ system at several temperatures. These were computed by fitting experimental values [1] of $\langle x^2 \rangle_T$ for ^{119}Sn to the theoretical expression Eq. (3). The neutron deter-

mined density of state for Pd at 120K and at 296 K was taken from the
work of MILLER and BROCKHOUSE [4].

Our value of the mass-weighted force constant i.e. A/M for Pd comes
out to be 8.28×10^{26} rad^2 sec^{-2}. This value was used in fitting of Eq. (3) to the
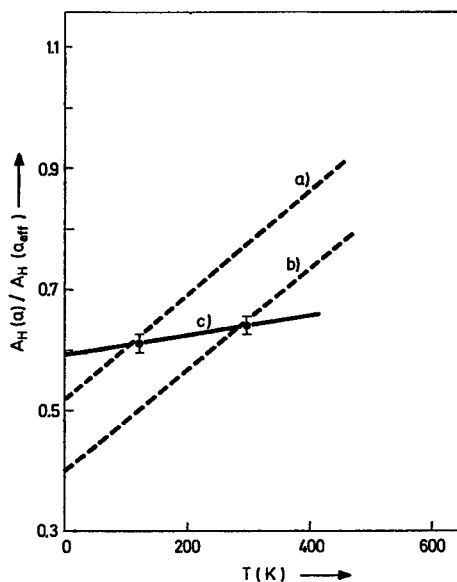Mössbauer f measurements [1]. We did include the corresponding maximum

Fig. 1. Effective host-host to impurity-host force constant ratio from Eq. (6) for $Pd_{0.99}$ $Sn_{0.0}$
as a function of temperature. The broken lines (a) and (b) result from fitting a wide temperature
range of f-values using $G(\omega)$ at 120K and 296K, respectively. The solid line (c) is obtained by
fitting the f-values only for those temperatures T_i at which each $G\omega(T_i)$ was determined,
i.e. 120 and 296K. The best value of A/A' is the $0-K$ intercept.

frequencies of $G(\omega)$, the frequency of the localised mode, and the fraction of
phonon states in the localised mode.

Each of the two broken lines (a) and (b) in Fig. 1 represent the results
of attempting to fit $\langle x^2 \rangle_T$ values at various temperatures using a fixed phonon
density of state [4] $G(\omega)_{T_o}$, measured at a single temperature $T_0[(a)T_0 = 120$ K
and (b) $T_0 = 296$ K].

The solid line (c) in Fig. 1, on the other hand, is obtained by fitting each
value of $\langle x^2 \rangle_{T_i}$ using a $G(\omega)_{T_i}$ determined from neutron scattering work at
that particular temperature T_i. The slope of the solid line gives $\Delta \varepsilon = \varepsilon_l - \varepsilon_h =
= (1.8 \pm 0.02) \times 10^{-4}$ K^{-1} and its 0-K intercept gives $A_H(a)/A'_H$ $(a_{eff}) =
= 0.59 \pm 0.01$ or $A'/A = 1.69 \pm 0.03$. This result is considerably different
from the finding of PURI and GUPTA [4], wherein they combined a Debye
spectrum with MANNHEIM's theory and neglected the anharmonic effects.

4. Discussion

We present here arguments as to why the preceding method of analysis of force constant evaluation is really meaningful.

On examining Eq. (6), one finds that the ratio $A_{eff}(T)/A'_{eff}(T)$ which is obtained from a fit to the experimental data [1] at various temperatures gives only the difference in anharmonicity i.e. $\varepsilon_i - \varepsilon_h = \Delta\varepsilon$ between the pure and impure systems. The significance of the solid line lies in the fact that its slope is a measure of this difference. Presently neutron data for Pd host is available only at two temperatures, therefore, any other point is not ascertained to make the solid line in Fig.1 look more meaningful. Moreover, in systems where the quantity $A_H(a)/A'_H(a_{eff})$ [Eq. [6]] can be obtained from an extrapolation to $T = 0$ of the fitted parameters $A_{eff}(T)/A'_{eff}(T)$, the former force constant ratio has now an unambiguous meaning within the framework of any harmonic lattice model. It is also clear that in the absence of data on anharmonicity in the pure crystal, precision recoilless fraction measurements can yield information about the difference $\varepsilon_i - \varepsilon_h = \Delta\varepsilon$ between the impure system and the host lattice.

The reason as to why our value of A/A' falls in the range reported by LANDUYT et al (0.60 ± 0.10) lies in the fact that the system may well be anharmonic, but if $\Delta\varepsilon$ is small, this difference may not show up in the force-constant ratio A/A' evaluated at different temperatures. In fact such a case has also been observed for ^{57}Fe impurity in Pd host [8]. Rather it needs to be emphasized that the suggested procedure of using the phonon frequency distribution $G(\omega)_T$ evaluated at the same temperature for which the Mössbauer impurity measurement is made, greatly reduces the temperature variation in the predicted force constant ratios. The force constant ratios so obtained have a more clearly defined physical significance and their changes with temperature truly reflect differences in behaviour between the host impurity and host-host systems.

We conclude that further improvement in the reliability of reported value(s) of force constant ratios could result if additional low-temperature neutron-dispersion studies in several host metals in which anharmonic effects presently contribute to uncertainities are made. On the other hand precision Mössbauer measurements could also remove certain inconsistencies in the impurity data.

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