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Determination of an unambiguous parameter for the impurity-lattice interaction*

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Experimental data analyzed with harmonic theories have established that generally the force constants between impurities and pure lattice differ from those of the host. However, the meaning of most reported impurity-host force-constant ratios is ambiguous for various reasons, one of which is that anharmonic effects are not properly accounted for. A method is outlined which leads to a well-defined interaction parameter, provided sufficient data are available for the impurity system. For highly dilute Fe in Cu and Fe in Pd we find an effective nearest-neighbor impurity host to host-host force-constant ratio $A'_H(a_{\mathrm{eff}})/A_H(a) = 1.31 \pm 0.03$ and 0.60 ± 0.01, respectively.

I. INTRODUCTION–IMPURITY-LATTICE PROBLEM

The dynamics of impurity atoms in crystal lattices have been the object of many experimental, as well as theoretical studies in the past ten years. The experimental tools which have been used to study impurity-lattice dynamics in metals, in particular, are inelastic neutron scattering, differential-specific-heat measurements, and the Mössbauer effect. Various models of the impure crystal have been utilized in the literature to extract information on effective impurity-host to host-host force-constant ratios. These range from simple modifications of the Debye model to a few considerably more realistic models, incorporating symmetries, polarizations, and modified impurity-host forces, in addition to the effects due to the altered mass.

The mathematical complexity of the theoretical problem, caused by the broken translational symmetry, has severely limited the physical realism of all but the most sophisticated of these models. In order to make any of these impurity theories amenable to numerical analysis (and thus useful for quantitative interpretations of experiments) the following simplifying assumptions have had to be made: (i) the impurity-lattice interaction is *harmonic;* (ii) changes in interatomic interactions are limited to the cluster of *nearest-neighbor atoms* about the impurity, all other interactions between host and impurity remaining the same as those in the pure host crystal; (iii) only *isolated impurities* need to be considered (no neighboring impurity atoms). Only the Mössbauer resonance technique allows investigation of "isolated" impurities in extremely-low-concentration alloys. The poor sensitivity of inelastic-neutron-scattering and specific-heat measurements to the effects of impurity atoms, imposes a lower limit of several atomic percent on the impurity concentrations which can be investigated, while most Mössbauer studies are done with alloys in the 10^{-4} to 10^{-2}-at.% ranges where probabilities for impurity-impurity neighbors are negligible.

In spite of its unphysical properties, the Debye model is still most often used in the literature for the analysis of impurity dynamics, presumably because of its ease of application. Applied to measurements of various quantities of *pure* materials (like specific heat, Debye-Waller factor, etc.), the Debye model gives indeed fair agreement with experiments, provided one disregards variations of as much as 20% between the frequencies characteristic for *different* physical quantities of the *same* system. Also, the characteristic Debye frequency for any particular quantity of a material often varies rapidly with temperature by a similar amount, especially at low temperatures. Being a continuum model (an extrapolation of the long-wavelengths limit for a discrete lattice), the Debye model ignores all effects due to crystal structure, as well as all features related to particular polarizations and propagation directions of the phonons. *Thus the Debye model is very useful for quick estimates and qualitative discussion,* though it is illsuited for detailed lattice-dynamical studies. The various ambiguities and confusions arising from use of the Debye model for evaluations of lattice-dynamical quantities were discussed in detail ten years ago by Salter[1] and others. Moreover, an impurity in a lattice site has features of a coupled oscillator, exhibiting a vibrational response dominated by certain resonances. Conceptually, therefore, a Debye density-of-states function does not describe the response of an impurity very well. Thus, a physical interpretation in terms of force-constant changes, derived from the characteristic frequency, which in turn was obtained by fitting impurity data to a Debye distribution, is at best problematical. Considerable improvement for such an interpretation can be gained by the introduction of the appropriately *weighted* Debye frequencies for host and impurities, since these can be related to the moments of the *real* distribution functions.[1,2]

Several more sophisticated theories, incorporating symmetry and phonon polarization, as well as a physically reasonable representation of the resonance nature of the impurity motion, have been proposed in the past.[3,4] One that is particularly useful for the experimentalist, though often overlooked, is the impurity theory developed by Mannheim *et al.*[4,5] The unique and most valuable feature of their model is the fact that its final expressions for the dynamical quantities of the impurity are *analytical* and independent of the crystal structure.[6] This important simplification was achieved at the price of considering strictly *central forces* in addition to the aforementioned restrictions. For the evaluation of measurable quantities for an impurity, one needs to know in general the force constants and the corresponding phonon density of states $G(\omega)$ for the *pure* material, in combination with the known impurity-host mass ratio M'/M. The usually unknown effective nearest-neighbor impurity-host force constant A' can then be obtained as a fitting parameter from experimental data.

When an attempt is made to study regularities or trends of impurity-host force-constant changes in various systems, serious discrepancies as well as ambiguities in the many reported data become apparent. These are at least in part due to the use of widely differing simplifications in the theoretical models, inappropriate or inaccurate data for the pure materials (e.g., Debye temperatures from inappropriate measurements) and various methods of data analysis. An additional source of ambiguity, even where a realistic impurity theory (as well as host data) was used, arises from a neglect of (or an oversimplified correction for) *anharmonic effects,* which influence, in particular, high-temperature data. In the remainder of this paper, we will focus primarily on the nature of this specific problem as it affects the interpretation of Mössbauer studies of highly dilute alloys. We will suggest methods of data analysis which can avoid or minimize the ambiguities due to anharmonicity. Our discussions will be given within the framework of Mannheim's impurity theory.[4,5] This choice was made on the basis of the model's analytical form. We propose that the suggested procedure represents the best present compromise between available experimental data and those theoretical models which are suitable for their evaluation in terms of a change in the effective nearest-neighbor impurity-host force constant with minimum ambiguity.

II. EFFECTIVE NEAREST-NEIGHBOR IMPURITY-HOST TO HOST-HOST FORCE-CONSTANT RATIO A'/A

For many pure metals the density of states $G(\omega)$ can be obtained from inelastic neutron scattering studies, mostly performed at room temperature. In contrast to the limitations imposed on the impurity problem by the broken translational symmetry, the models employed to analyze *pure* host lattices generally include up to sixth or higher-neighbor force constants, sometimes limited by certain constraints (central forces, axially symmetric forces, etc.), but often only limited by general symmetry considerations for the particular lattice. The various force constants are then evaluated by numerical fitting to elastic constants and to neutron dispersion curves for various symmetry directions of the crystals.[7] These results, in turn, yield rather realistic and detailed phonon densities of states $G(\omega)_T$, representative of the temperature T at which the scattering experiments were performed.[8] Using such a density of states function for the host in the theoretical expressions of the impurity theory,[4,5] and allowing the effective force-constant ratio[9] A'/A to vary, a fit to experimental dynamical quantities of the impurity (e.g., $\langle x^2\rangle_{\text{imp}}$) measured at the same temperature T, can be obtained. A' and A are defined in Sec. IV, Eq. (2). They represent the effective-nearest-neighbor force constants, connecting impurity-to-host and host-to-host atoms, respectively. Systematic studies of A'/A for Fe in a variety of host crystals have been attempted in the literature,[10] but trends were in part masked by the ambiguities and inaccuracies alluded to in Sec. I, thus casting doubt on some conclusions. This is particularly serious since the variations in the values A'/A for various impurity systems generally fall within a range similar in magnitude to the relative error introduced by those inaccuracies.

For a real crystal both A and A' will in general be functions of temperature, due to anharmonicity. This feature has been studied in detail in several pure materials for which neutron dispersion curves were obtained at several temperatures.[11] The changes of the various force constants with increasing temperature differ widely from each other, leading not only to a general shift toward lower frequencies of the band edge $\omega_{\max}$, but also to a *nonuniform* change of the distribution $G(\omega)$. This is in contrast to the usual assumption of the quasi-harmonic approximation in which $G(\omega)$ is assumed to *scale* linearly with T. It is therefore reasonable to expect that the impurity-host force constants are similarly temperature dependent.

III. UNAMBIGUOUS EVALUATION OF A'/A FROM MÖSSBAUER EXPERIMENTS

In various Mössbauer impurity studies, the zero-phonon fraction $f(T)$ was measured with great accuracy in order to obtain mean-squared displacements $\langle x^2\rangle_T$ at various temperatures. From these, effective force constant ratios A'/A can be derived. In some studies line shifts were measured as a function of temperature instead of, or in addition to, $\langle x^2\rangle_T$. From these shifts another dynamical quantity, the mean-squared velocity $\langle v^2\rangle_T$, can be derived, in principle. However, greater uncertainties are inevitable in these latter studies, due to admixture of other effects such as chemical shift, whose temperature dependences are unknown.

The procedure commonly followed in the past has been to attempt to fit a set of data points which cover a wide temperature range to a "best" curve as predicted by a harmonic impurity model. If Mannheim's impurity theory is used in combination with a density of states function for the host $G(\omega)_{T_0}$ obtained at one temperature T_0 (usually room temperature) from neutron dispersion relations, *none* of the theoretical curves for $\langle x^2\rangle_T$ for various assumed values of the force constant parameter A'/A fit *precision* data points very well,[12,13] except in experimental studies limited to low temperatures.[14] In a recent high-precision study of the mean-squared displacement of Fe in Cr it was clearly shown[15] that the data could not be fitted by the harmonic impurity theory[4,5] using $G(\omega)_{300\,\mathrm{K}}$ for the host and a *temperature-independent* force-constant ratio A'/A. Extending the results of a study of anharmonic effects in pure materials by Maradudin and Flinn,[16] a similar relation for the anharmonic contribution to the mean-squared displacement of an impurity was postulated.[17-19]

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

where $\langle x^2\rangle_T^H$ was assumed to correspond to the value as predicted by the harmonic theory. Recently, with the aid of Mannheim's theory,[4,5] excellent agreement with data could be obtained over a wide temperature range by a *two-parameter* fit[20] involving the force constant ratio A'/A as well as the anharmonicity parameter ϵ from Eq. (1). However, force-constant ratios A'/A so obtained remain ambiguous in their physical interpretation. The reason is that the parameter ϵ, and thus also the co-fitted value obtained for 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 lattice relaxation effects due to the introduction of the impurity (see Sec. IV and *Note added in Proof* of Ref. 20).

We suggest in this paper instead, that for host systems where neutron data are available at *various temperatures* T_i, the mean-squared displacement $\langle x^2\rangle$ of the impurities should be measured with high precision especially at those same temperatures T_i. This will assure consistency with the assumptions made in the impurity theory.[4,5] The different force-constant ratios $(A'/A)_{T_i}$ so obtained from a *single-parameter* fit to the experimental value may still contain various implicit temperature-dependent effects. However, we will show below that for these impurity systems such complications can be eliminated and an unambiguously defined impurity-host force-constant ratio can be obtained.

It can be shown[21] that at any given temperature, within the range of temperatures at which reliable neutron scattering data are presently available, the inverse ratio A/A' is proportional to $\langle x^2\rangle_T$. This, coupled with Eq. (1), lead us to expect a linear relationship between A/A' and temperature. The following discussion, therefore, pertains to this inverse ratio A/A' for which we propose, in the absence of a detailed theory of its low-temperature behavior, a linear extrapolation to low temperatures in Sec. IV. For those hosts where neutron data are available only at *one temperature* T_0, while impurity data cover a large temperature range, both above and below T_0, only *upper* and *lower bounds* should be reported for A/A' (see Sec. IV).

IV. THEORETICAL BASIS OF THE METHOD

A. Definition of A and A'

We propose in this section to differentiate between two types of force constants for the host crystal: a *harmonic* one which we denote by $A_H(a)$ and a "real" or effective force constant $A_{\mathrm{eff}}(T)$. The definition of $A_H(a)$ in terms of the second derivative of the potential for a cubic lattice[4,5] 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. $A_H(a)$ therefore physically represents the restoring force in the x direction for a unit displacement in the x direction of an atom at the origin, while the other atoms in the crystal are held fixed at their equilibrium positions. Although in the Mannheim theory, the summation in Eq. (2) extends to nearest neighbors only, the parameter $A_{xx}(0,0)$ is unambiguously defined as a sum over *all* atoms in the crystal. As Mannheim has pointed out,[5] the assumed proportionality between $A_H(a)$ and $\omega^2_{\max}$ 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 neighbors;* it must be modified if more distant neighbors are included. The force constant $A_{xx}(0, 0)$, however, is uniquely defined for *any* lattice model, including nth-neighbor interactions, from which $G(\omega)$ has been obtained. Therefore, the actual value of $A_{xx}(0, 0)$ for the host (see Table I) should be used in the theoretical expressions rather than $\frac{1}{2}M\omega^2_{\max}$ for the numerical evaluation of the dynamic response function $G'(\omega)$ of the impurity[4,5,20]

$$\langle x^2\rangle_T = \frac{\hbar}{2M'}\int_0^\infty \omega^{-1}\coth\left(\frac{\frac{1}{2}\hbar\omega}{k_BT}\right)G'(\omega)\,d\omega\,, \tag{3a}$$

with

$$\begin{aligned}G'(\omega) = {} & (M/M')G(\omega)\{[1+\rho(\omega)S(\omega)]^2 \\ & +[\tfrac{1}{2}\pi\omega G(\omega)\rho(\omega)]^2\}^{-1} + \delta(\omega-\omega_L)(M/M') \\ & \times\{\rho^2(\omega)T(\omega)+(M/M')-[1+\rho(\omega)]^2\}^{-1}\,,\end{aligned} \tag{3b}$$

where

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

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

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

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

B. Anharmonic effects

In keeping with the usual procedures, we absorb lattice expansion effects in $A_H(a)$, and in $A_{\text{eff}}(T)$ we include any other anharmonic effects. Following similar reasoning as for the mean-squared displacement [Eq. (1)], it is therefore physically appropriate to relate these effects to the measured force constants in the following manner:

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

where ϵ_h now describes the combined anharmonic contributions to the force constants [Eq. (2)] in the host. Higher terms in such an expansion were shown to be negligible.[16]

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

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

TABLE I. Contributions to $A_{xx}(0, 0)$ from a sixth nearest-neighbor model for Cu at 296 K.

Component [a] designation	Value [b] (10^4 dyn/cm)	Number of atoms contributing	Total contribution
α_1^1	1.3178	8	10.5424
α_3^1	−0.1404	4	−0.5616
α_1^2	0.0218	2	0.0436
α_2^2	−0.0191	4	−0.0764
α_1^3	0.0628	8	0.5024
α_2^3	0.0283	16	0.4528
α_1^4	−0.0017	8	−0.0136
α_3^4	−0.0187	4	−0.0748
α_1^5	−0.0094	8	−0.0752
α_2^5	−0.0043	12	−0.0516
α_3^5	−0.0038	4	−0.0152
α_1^6	−0.0037	8	−0.0296

$$A_{xx}(0, 0) = 10.6432\times10^4\ \text{dyn/cm}$$

$$\frac{1}{M}A_{xx}(0, 0) = 10.09\times10^{-26}(\text{rad/sec})^2$$

[a] Notation is that of Ref. 7. [b] From data in Ref. 22. see Sec. V.

In this equation the primes denote the changed values of the force constant and ϵ_i stands for the anharmonic parameter in the presence of the impurity. Also, in the impure system we denote the lattice constant by $a_{\rm eff} = a + \delta a_0$, where δa_0 is a small change due to relaxation of the lattice upon alloying at $T = 0$ K. Being mainly a size effect, δa_0 is assumed in first approximation to be independent of temperature.

The force-constant ratio A/A' [Eq. (3c)] appearing in the impurity theory[4, 5] is the ratio $A_{\rm eff}(T)/A'_{\rm eff}(T)$; therefore, we write

$$\frac{A_{\rm eff}(T)}{A'_{\rm eff}(T)} = \frac{A_H(a)(1-\epsilon_h T)}{A'_H(a_{\rm eff})(1-\epsilon_i T)} \, . \tag{5}$$

It is well established[16] that typical anharmonicity parameters are of order 10^{-4} K^{-1}, so that we can safely expand the denominator in Eq. (5) to obtain

$$\frac{A_{\rm eff}(T)}{A'_{\rm eff}(T)} = \frac{A_H(a)}{A'_H(a_{\rm eff})}\left[1 + (\epsilon_i - \epsilon_h)T + O(\epsilon_i \epsilon_h)\right] . \tag{6}$$

C. Interpretation

An important conclusion can be drawn from Eq. (6): the ratio $A_{\rm eff}(T)/A'_{\rm eff}(T)$ which can be obtained from a fit to the experimental data at various temperatures can only indicate the *difference* in anharmonicity $\Delta\epsilon = \epsilon_i - \epsilon_h$ between the pure and the impure systems. The system may well be anharmonic, but if $\Delta\epsilon$ vanishes, this anharmonicity will not show up in the force-constant ratios evaluated at different temperatures. In fact, as is discussed below, such appears to be the case for the highly dilute Pd(Fe) alloy.

A simple model would predict that the introduction of point defects into a perfect lattice will enhance anharmonic effects; on that basis $\Delta\epsilon$ is expected to be positive. However, negative values may well occur in certain systems, (see *Note added in proof*).

As a consequence of the use of oversimplified impurity models and/or an inadequate consideration of the various temperature dependent effects, most of the reported anharmonicity parameters for impurity systems[15, 17–20] are of the correct order of magnitude but they are conceptually only vaguely related to $\Delta\epsilon$ as defined in Eq. (6).

The second important conclusion to be drawn from Eq. (6) is that in systems for which the quantity $A_H(a)/A'_H(a_{\rm eff})$ can be obtained from an extrapolation to $T = 0$ of the fitted parameters $A_{\rm eff}(T)/A'_{\rm eff}(T)$, the former force-constant ratio now has an unambiguous meaning within the framework of any harmonic lattice model.

V. APPLICATION TO Cu(Fe) AND Pd(Fe) SYSTEMS

In Fig. 1 we show values of $A_{\rm eff}(T)/A'_{\rm eff}(T)$ for highly dilute Cu(Fe) at several temperatures. These were obtained from fitting experimental values of $\langle x^2\rangle_T$ for Fe^{57} (as obtained from precision Mössbauer f measurements[19]) to the theoretical expression Eq. (3). The density of states at each temperature was obtained by fitting the dispersion curves from recent neutron-scattering studies[22, 23] to Born–von Kármán theory. In each case the same model was used to obtain force constants up to sixth nearest neighbors in order to remove any dependence on the different models employed by the various investigators themselves.

The evaluation of $A_{xx}(0, 0)$ in terms of these force constants is given in Table I.

In Table II we list the mass-weighted force constants A/M for Cu and Pd at various temperatures which were used in the fitting of Eq. (3) to the Mössbauer f measurements at these temperatures. We also included the corresponding maximum frequencies of $G(\omega)$, the frequency of the localized

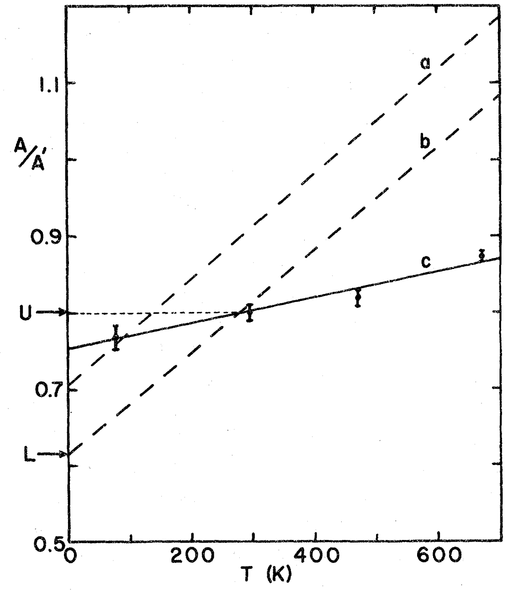

FIG. 1. Effective host-host to impurity-host force-constant ratio, A/A' from Eq. (6), for highly dilute Fe in Cu from Mössbauer fraction measurements, neutron-inelastic-scattering data, and Mannheim's impurity model, as a function of temperature. The broken lines result from fitting a wide temperature range of f values using $G(\omega)_T$ obtained at a *single* temperature [curve (a) $G(\omega)_{80\,{\rm K}}$; curve (b) $G(\omega)_{296\,{\rm K}}$]. 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 obtained. The "best" value of A/A' is the 0-K intercept. L and U show the lower and upper bounds, respectively, to A/A' that could be obtained if only the $G(\omega)_{296\,{\rm K}}$ were available.

TABLE II. Dynamical parameters for Cu and Pd at various temperatures.

Metal	T (K)	A/M (10^{26} rad^2/sec^2)	$\omega_{\max}$ (10^{13} rad/sec)[a]	A/A'[b]	ω_L (10^{13} rad/sec)[c]	Fraction of states in local mode
Cu	80	10.563	4.675	0.78 ± 0.03	4.790	38%
Cu	296	10.091	4.645	0.81 ± 0.02	4.659	23%
Cu	473	9.577	4.595	0.84 ± 0.02	none	···
Cu	673	9.300	4.555	0.89 ± 0.02	none	···
Pd	120	8.470	4.380	1.70 ± 0.03	none	···
Pd	296	8.193	4.355	1.67 ± 0.02	none	···
Pd	673	7.607	4.275	1.67 ± 0.02	none	···

[a] $\omega_{\max}$ is the maximum phonon frequency in the host distribution function.
[b] A and A' are the effective force constants as defined by Eqs. (2) and (3c).
[c] ω_L is the frequency of the localized vibrational mode (if present).

mode, and the fraction of phonon states in the localized mode. Note the interesting fact that for Fe in Cu the impurity theory predicts a localized mode at low temperatures, which disappears rapidly above room temperature.

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 states $G(\omega)_{T_0}$, measured at a single temperature T_0 [(a) $T_0 = 80$ K and (b) $T_0 = 296$ K]. As has been discussed above, this procedure leads to a force-constant ratio that changes significantly with temperature. 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, and it therefore corresponds to the procedure suggested at the end of Sec. IV. The slope of the solid line gives $\Delta\epsilon = (1.6 \pm 0.4)\times 10^{-4}$ K^{-1}, and its intercept $A_H(a)/A'_H(a_{\text{eff}}) = 0.76 \pm 0.02$ or $A'/A = 1.31 \pm 0.03$. This result differs appreciably from a recent reevaluation[24] of older data[17] in which anharmonic effects were neglected. The present value of A'/A should also be preferred over that reported recently by us on the basis of a less clearly defined procedure.[20]

From Fig. 1 we can also see how to obtain estimates of *upper* and *lower bounds* to the force constant ratio A/A' when $G(\omega)_{T_0}$ is known at one temperature T_0 only. Assuming that $\Delta\epsilon$ is likely to be positive (Sec. IV C), a calculation of $A_{\text{eff}}(T_0)/A'_{\text{eff}}(T_0)$ will yield a value *greater* than $A_H(a)/A'_H(a_{\text{eff}})$ and will give an *upper bound* to A/A' (U in Fig. 1). On the other hand, by fitting $\langle x^2\rangle_T$ at various temperatures using a fixed $G(\omega)_{T_0}$ and extrapolating $(A/A')_T$ to 0 K, a *lower bound* to A/A' may be estimated (L in Fig. 1). However, the assumption of a positive $\Delta\epsilon$ is uncertain. Additional neutron studies, performed at low temperatures, would help to reduce appreciably the range of uncertainty in the extrapolated A/A' values (see *Note added in proof*).

Neutron studies have also been performed at several temperatures[22] for Pd. We have reanalyzed our data[19] using the impurity theory[4,5] and Eq. (6) for this system to obtain the values listed in Table II, from which we deduce $[A_H(a)/A'_H(a_{\text{eff}})]_{\text{av}} = 1.68 \pm 0.02$ or $A'/A = 0.60 \pm 0.01$, in rather good agreement with our former method of analysis.[20] This value differs appreciably, however, from a recent evaluation of absorber data,[25] in which impurity theory[4] was combined with *Debye spectra* for the host metals. This case is an example of the vanishing of $\Delta\epsilon$ within the limits of error although ϵ_h, which can be estimated from the data given in Ref. 22, is approximately 2.0×10^{-4} K^{-1}.

It should be pointed out that the nonvanishing $\Delta\epsilon$ for the Cu:Fe system does not *necessarily* represent a different temperature dependence between host-impurity and host-host nearest-neighbor force constants. Such an effect could also result from changes in the relative contributions from more distant neighbors and/or noncentral forces which do not appear in the theory. Indeed, studies of the temperature dependence of phonons in pure materials show different relative shifts for differing directions of propagation and polarization, which in turn result from variations in the temperature dependences of near and more distant neighbors.[11] On the other hand, Born–von Kârmân theory indicates that the nearest-neighbor central force constant is dominant for Cu: none of the noncentral or more distant neighbor forces contribute more than 5% to $A_{xx}(0,0)$ (see Table I). The point is that we do not wish to place too much significance in the precise value of $\Delta\epsilon$. Rather we wish to emphasize that the suggested procedure of using the distribution $G(\omega)_T$ evaluated at the same temperature for which the impurity data were obtained, greatly reduces the temperature variation in the predicted force constant ratios by properly including the effects of temperature changes in the host lattice. The force constant ratios thus obtained have a more clearly defined physical significance than previously reported values, and their changes with temperature truly reflect differences in behavior between the host-impurity and host-host systems.

Similar reevaluations in terms of $A_H(a)/A'_H(a_{\text{eff}})$ of available force-constant data on other impurity systems are at present hampered by a lack of neutron scattering data on pure crystals at low temperatures. For those cases, only upper and lower bounds can confidently be determined.

VI. CONCLUSION

We suggest a method of analysis of Mössbauer data on dilute alloys which takes into account the anharmonic effects in the pure host provided neutron data at several temperatures are available. Combining an analytical and physically reasonable impurity theory with the best available data on the pure-host phonon density of states, a well-defined value for the effective nearest-neighbor impurity-host to host-host force-constant ratio can be obtained. A uniform treatment of all available data along the suggested lines would greatly reduce the present ambiguities in published values and is essential to a study of systematic trends of impurity behavior in various hosts.[21]

We have also shown that in the absence of data on anharmonicity in the pure crystal, precision Mössbauer fraction measurements can only yield information about the *difference* $(\epsilon_i - \epsilon_h)$ between the impure system and the host lattice.

Note added in proof: Recent data[14] on ^{197}Au in Cu yield $A'/A \simeq 1.6$, using host and impurity data at 49 K and 80 K, possibly with a negative value of $\Delta\epsilon$.

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