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Lattice dynamics of PdD_x and PdH_x

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Abstract. Lattice dynamics of PdD_x and PdH_x are analysed with reference to the coherent neutron scattering experiments of Rowe *et al* and incoherent neutron scattering lineshape reported by Rahman *et al*. Disorder in the octahedral interstitial sublattice is treated within a coherent potential approximation format suitable for treating both 'on-site' and 'off-diagonal' randomness. Our results lead to a substantial readjustment (upwards) in the accepted values of the D–D potential. Moreover, an adjustment (downwards) is also indicated in the published value of the Pd–H potential.

1. Introduction

Investigations of metal hydrides have received a great impetus as a result of the widening technological application of these systems (see for example, Reilly and Sandrock 1980). In particular, the mixed system palladium–hydrogen (deuterium) displays a great richness of interesting physical phenomena. For example, amongst its properties are the following that have elicited careful attention: the incoherent response of the diffusing hydrogen atoms (Sankey and Fedders 1979); dynamics of spinodal decomposition (Manchester 1982); and its fascinating superconducting behaviour (Stritzker 1982). Not surprisingly, the superconductivity of the Pd–H and Pd–D system is found to be strongly dependent upon their phonon spectra. Accordingly, it is interesting to examine the phonon density of states of these mixed systems.

Palladium has FCC structure. When deuterium (or hydrogen) is introduced, it occupies interstitial octahedral sites. PdD_x presents two phases: namely, the so-called α and β phases, each with its own different lattice parameter and deuterium content. The α phase has approximately the same lattice parameter as that of pure Pd and obtains at low D concentration. The β phase appears at high concentration of D and the relevant lattice parameter is about 5% larger than that for the α phase (see for example, Mueller *et al* 1968).

An important feature of interstitial mixtures is that the impurity atoms generally do not replace the host atoms. Rather, they arrive as an addition which increases random-

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ness in the system as well as its available degrees of freedom. Accordingly, it is both more convenient and more accurate to evolve a formulation for treating interstitial randomness as distinct from one which only handles substitutional disorder.

For the particular case of palladium–hydrogen or palladium–deuterium alloy, with its attendant vast differences in the masses of the two constituent atoms, the presence of hydrogen or deuterium atoms gives rise to prominent optical branches in the phonon spectra. In addition to this important effect, the lattice itself experiences substantial local strain due to the light-atom occupancy, which gets felt beyond the nearest-neighbour shell. Consequently, the PdD_x and PdH_x systems involve both ‘diagonal’ and ‘off-diagonal’ disorders, the latter being carried farther than the neighbouring shell. The bulk of the diagonal disorder, however, is specific to the single site itself, related as it is to mass randomness. Accordingly, the ‘environmental dependence’ of the diagonal disorder has the following rather desirable characteristics: (a) much of the diagonal disorder, related to mass randomness, has no environmental dependence; and, (b) the component with environmental dependence has a large number of effective neighbours. Consequently, the latter is amenable to a mean-field-like approximation of the environment. These features make it possible to treat the PdD_x problem in a simple framework, constructed from a generalisation of the Blackman, Esterling and Berk (1971) version of the coherent potential approximation (BEB-CPA). For notational convenience the present generalisation is referred to as ISCPA, meaning a CPA which can be applied to systems with interstitial as well as substitutional disorder. An alloy with simple substitutional randomness has recently been studied by two of us (Sansores and Tagüena-Martinez 1981). Here it is convenient to develop a formulation applicable to the general case in which substitutional as well as interstitial disorder may be present. Such a formulation is essential for treating mixed systems of the variety $\text{Pd}_y\text{Ag}_{1-y}\text{D}_x$ (to be discussed in a forthcoming paper). On the other hand, in the present paper we shall restrict ourselves to the analysis of the somewhat simpler systems, PdD_x and PdH_x , which contain only interstitial disorder.

2. Formulation

It is convenient to work within a two-sublattice framework, familiar in the context of antiferromagnetism. One of the sublattices is reserved for the host lattice and the other for the interstitials. Whenever the interstitial sublattice is either empty (i.e. all its sites are vacant) or is completely full (i.e. has no vacancies) and the host sublattice includes substitutional randomness (due to the replacement of some of the host atoms by impurities), we recover the case of substitutional disorder treated within the BEB-CPA. On the other hand, if the interstitial sublattice is random, but the host sublattice possesses translational symmetry, we have the case of simple interstitial disorder. Both for such a system and for the more general one where randomness occurs in the host as well as the interstitial sublattices, the following generalisation of the BEB-CPA, i.e. ISCPA, may be used.

We write the Hamiltonian in its harmonic form:

$$\mathcal{H}(t) = \sum_{\alpha\sigma} \frac{1}{2} (P_{\alpha}^{\sigma}(l, t))^2 / M_{\alpha}^{\sigma}(l) + \frac{1}{2} \sum_{\substack{\alpha\alpha' \\ \sigma\sigma' \\ ll'}} U_{\alpha}^{\sigma}(l, t) \varphi_{\alpha\alpha'}^{\sigma\sigma'}(l, l') U_{\alpha'}^{\sigma'}(l', t). \quad (1)$$

Here l denotes atomic location, σ is the sublattice index (i.e. $\sigma \equiv 1$ or 2) and α represents

the cartesian component, i.e. $\alpha \equiv x, y, z$. It is convenient to define the following commutator Green function (see for example, Elliott *et al* 1974).

$$G_{\alpha\alpha'}^{\sigma\sigma'}(l, l'; t) = (2\pi/\hbar) \langle\langle U_{\alpha}^{\sigma}(l, t); U_{\alpha'}^{\sigma'}(l', 0) \rangle\rangle. \quad (2)$$

Using the Hamiltonian (1), we can readily find the relevant equation of motion for G , i.e.

$$M_{\alpha}^{\sigma}(l) \omega^2 G_{\alpha\alpha'}^{\sigma\sigma'}(l, l'; \omega) = \delta_{\alpha\alpha'} \delta_{\sigma\sigma'} \delta_{ll'} + \sum_{\alpha''\sigma''} \varphi_{\alpha\alpha'}^{\sigma\sigma'}(l, l'') G_{\alpha''\alpha'}^{\sigma''\sigma'}(l'', l'; \omega). \quad (3)$$

It is, however, convenient to recast this as follows:

$$G_{\alpha\alpha'}^{\sigma\sigma'}(l, l'; \omega) = g_{\alpha}^{\sigma}(l) \delta_{\alpha\alpha'} \delta_{\sigma\sigma'} \delta_{ll'} + g_{\alpha}^{\sigma}(l) \sum_{\alpha''\sigma''} \varphi_{\alpha\alpha'}^{\sigma\sigma'}(l, l'') G_{\alpha''\alpha'}^{\sigma''\sigma'}(l'', l'; \omega), \quad (4)$$

where the notation $g_{\alpha}^{\sigma}(l)$ is used to indicate the bare locator, i.e.

$$g_{\alpha}^{\sigma}(l) = [M_{\alpha}^{\sigma}(l) \omega^2]^{-1}. \quad (5)$$

Note that so far the type of occupancy of the site l is implicit in the label l . It is, however, both necessary and convenient to introduce specific notation for the variety of atoms we may be dealing with. To keep the formulation general, we assume the host sublattice (henceforth to be called 1) to be composed of 'A' atoms originally and to admit 'A'' atoms as substitutional impurities. (Of course, if necessary, more than one type of substitutional impurity could be similarly treated.) The interstitial sublattice is considered to be composed of 'B' type of atoms. Finally, we denote the interstitial impurities as being of atomic variety 'B'''. (Once again, more than one type of such impurity could be treated.)

Within such a format, for brevity we denote the various interparticle potentials as follows:

$$\begin{aligned} \varphi_{\alpha\alpha'}^{11(22)}(i, j) &= \alpha^{11(22)}(i, j) \text{ if sites } i \text{ and } j \text{ are both occupied by A or (B) atoms} \\ &= \beta^{11(22)}(i, j) \text{ if sites } i \text{ and } j \text{ are both occupied by A' or (B') atoms} \\ &= \eta^{11(22)}(i, j) \text{ if site } i \text{ is occupied by A or (B) atom and site } j \text{ is occupied by} \\ &\quad \text{A' or (B') atom, or vice versa} \\ \varphi_{\alpha\alpha'}^{12}(i, j) &= \alpha^{12}(i, j) \text{ if site } i \text{ is occupied by an A atom and } j \text{ is occupied by a} \\ &\quad \text{B atom, or vice versa} \\ &= \xi^{12}(i, j) \text{ if site } i \text{ is occupied by an A atom and } j \text{ is occupied by a} \\ &\quad \text{B' atom, or vice versa} \\ &= \eta^{12}(i, j) \text{ if site } i \text{ is occupied by an A' atom and } j \text{ is occupied by a} \\ &\quad \text{B atom, or vice versa} \\ &= \beta^{12}(i, j) \text{ if site } i \text{ is occupied by an A' atom and } j \text{ is occupied by a} \\ &\quad \text{B' atom; or vice versa.} \end{aligned} \quad (6)$$

(To avoid confusion, cartesian labels α' , α'' have been suppressed in the terms on the right-hand side of equation (6).) Moreover, it is convenient to introduce the following atomic occupation variables, $X_{\alpha}(l)$ and $Y_{\alpha}(l)$:

$$\begin{aligned}
X_1(l) = 0, Y_1(l) = 0, X_2(l) = 0, Y_2(l) = 1, & \text{ if } l \text{ is occupied by a B' atom;} \\
X_1(l) = 0, Y_1(l) = 0, X_2(l) = 1, Y_2(l) = 0, & \text{ if } l \text{ is occupied by a B atom;} \\
X_1(l) = 0, Y_1(l) = 1, X_2(l) = 0, Y_2(l) = 0, & \text{ if } l \text{ is occupied by an A' atom;} \\
X_1(l) = 1, Y_1(l) = 0, X_2(l) = 0, Y_2(l) = 0, & \text{ if } l \text{ is occupied by an A atom.}
\end{aligned} \tag{7}$$

These occupation variables have the following important properties:

$$\begin{aligned}
X_\sigma(l)Y_\sigma(l) = 0; \quad X_\sigma(l)X_\sigma(l) = X_\sigma(l)\delta_{\sigma\sigma}; \quad Y_\sigma(l)Y_\sigma(l) = Y_\sigma(l)\delta_{\sigma\sigma} \\
\langle X_1(l) \rangle = c_A; \quad \langle X_2(l) \rangle = c_B; \quad \langle Y_1(l) \rangle = c_{A'}; \quad \langle Y_2(l) \rangle = c_{B'}
\end{aligned} \tag{8}$$

It is to be noticed that our choice of the occupation variables prevents atoms B and B' from being found in sublattice 1. Similarly, atoms A and A' cannot be present in sublattice 2.

If we now pre- and post-multiply equation (4) by $X_\sigma(l)$ and $Y_\sigma(l)$ we obtain the following set of equations. Written in a compact matrix form they become:

$$\mathbf{G}_{\alpha\alpha'}(l, l'; \omega) = \delta_{\alpha\alpha'} \mathbf{g}_\alpha(l) + \mathbf{g}_\alpha(l) \sum_{\alpha''} \mathbf{t}_{\alpha\alpha''}(l, l'') \mathbf{G}_{\alpha''\alpha'}(l'', l'; \omega). \tag{9}$$

For this representation we have utilised the notation given below:

$$\begin{aligned}
X_1(l)G^{11}(l, l'; \omega)X_1(l') &= G_{AA}^{11}(l, l'; \omega); & X_1(l)G^{12}(l, l'; \omega)X_2(l') &= G_{AB}^{12}(l, l'; \omega) \\
X_2(l)G^{21}(l, l'; \omega)X_1(l') &= G_{BA}^{21}(l, l'; \omega); & X_2(l)G^{22}(l, l'; \omega)X_2(l') &= G_{BB}^{22}(l, l'; \omega) \\
Y_1(l)G^{11}(l, l'; \omega)Y_1(l') &= G_{A'A}^{11}(l, l'; \omega); & Y_1(l)G^{12}(l, l'; \omega)Y_2(l') &= G_{A'B}^{12}(l, l'; \omega) \\
Y_2(l)G^{21}(l, l'; \omega)Y_1(l') &= G_{B'A}^{21}(l, l'; \omega); & Y_2(l)G^{22}(l, l'; \omega)Y_2(l') &= G_{B'B}^{22}(l, l'; \omega) \\
X_1(l)G^{11}(l, l'; \omega)Y_1(l') &= G_{A'A}^{11}(l, l'; \omega); & X_1(l)G^{12}(l, l'; \omega)Y_2(l') &= G_{A'B}^{12}(l, l'; \omega) \\
X_2(l)G^{21}(l, l'; \omega)Y_1(l') &= G_{B'A}^{21}(l, l'; \omega); & X_2(l)G^{22}(l, l'; \omega)Y_2(l') &= G_{B'B}^{22}(l, l'; \omega) \\
Y_1(l)G^{11}(l, l'; \omega)X_1(l') &= G_{A'A}^{11}(l, l'; \omega); & Y_2(l)G^{21}(l, l'; \omega)X_1(l') &= G_{B'A}^{21}(l, l'; \omega) \\
Y_1(l)G^{12}(l, l'; \omega)X_2(l') &= G_{A'B}^{12}(l, l'; \omega); & Y_2(l)G^{22}(l, l'; \omega)X_2(l') &= G_{B'B}^{22}(l, l'; \omega) \\
X_1(l)g^1(l) &= g_A^1(l); & X_2(l)g^2(l) &= g_B^2(l) \\
Y_1(l)g'(l) &= g_{A'}^1(l); & Y_2(l)g^2(l) &= g_{B'}^2(l).
\end{aligned} \tag{10a}$$

$$\mathbf{G}_{\alpha\alpha'}(l, l'; \omega) = \begin{pmatrix} G_{AA}^{11} & G_{AB}^{12} & G_{A'A}^{11} & G_{A'B}^{12} \\ G_{BA}^{21} & G_{BB}^{22} & G_{B'A}^{21} & G_{B'B}^{22} \\ G_{A'A}^{11} & G_{A'B}^{12} & G_{A'A}^{11} & G_{A'B}^{12} \\ G_{B'A}^{21} & G_{B'B}^{22} & G_{B'A}^{21} & G_{B'B}^{22} \end{pmatrix}_{\alpha\alpha'}(l, l'; \omega), \tag{10b}$$

$$\mathbf{t}_{\alpha\alpha''}(l, l'') = \begin{pmatrix} \alpha^{11} & \alpha^{12} & \eta^{11} & \xi^{12} \\ \alpha^{21} & \alpha^{22} & \eta^{21} & \eta^{22} \\ \eta^{11} & \eta^{12} & \beta^{11} & \beta^{12} \\ \xi^{21} & \eta^{22} & \beta^{21} & \beta^{22} \end{pmatrix}_{\alpha\alpha''}(l, l''), \tag{10c}$$

$$\mathbf{g}_\alpha(l) = \begin{pmatrix} g_A^1 & 0 & 0 & 0 \\ 0 & g_B^2 & 0 & 0 \\ 0 & 0 & g_{A'}^1 & 0 \\ 0 & 0 & 0 & g_{B'}^2 \end{pmatrix}_\alpha (l). \quad (10d)$$

(Again, it was convenient to suppress the cartesian labels in equation (10a). Note, in equation (10d), the possible occupancy of site l is reflected in the relevant matrix element that it entails.)

Once the compact relationship (9) has been evolved, it is straightforward to achieve a BEB-type configurational averaging. To this end we rewrite equations (3.11)–(3.13) of Blackman *et al* (1971) as follows:

$$\mathbf{U}_0[\gamma] = \gamma^{-1}[\mathbf{G}[\gamma]\mathbf{t}]_0 \quad (11)$$

$$\gamma = \langle \mathbf{g}(\mathbf{1} - \mathbf{U}_0[\gamma]\mathbf{g})^{-1} \rangle \quad (12)$$

and

$$\mathbf{G}_k[\gamma] = [\mathbf{1} + \gamma(\mathbf{U}_0[\gamma] - \mathbf{t}_k)]^{-1}\gamma. \quad (13)$$

The averaging process implicit in the above equations is now used in a similar fashion for the problem in hand. The only differences lie in the 4×4 dimensionality of the present formulation as well as the changes in the definition of the relevant matrices (see equations (10a)–(10d)).

As mentioned earlier, the above 4×4 formulation is essential to the analysis of systems such as $\text{Pd}_y\text{Ag}_{1-y}\text{D}_x$ (forthcoming). However, since in the present work the simpler systems PdD_x and PdH_x are being discussed, we particularise the remaining analysis to these systems. Consequently, the above system of equations can be cast into a set of three coupled equations:

$$\gamma^A = \left(\frac{1}{3N}\right) \sum_{k,j} [Q - \alpha_{BB}^{22}(k,j)]/D(k,j), \quad (14a)$$

$$\gamma^B = \left(\frac{1}{3N}\right) \sum_{k,j} [R - \alpha_{AA}^{11}(k,j)]/D(k,j), \quad (14b)$$

$$0 = \left(\frac{1}{3N}\right) \sum_{k,j} [U - \alpha_{AB}^{12}(k,j)]/D(k,j) \quad (14c)$$

where

$$D(k,j) = [R - \alpha_{AA}^{11}(k,j)][Q - \alpha_{BB}^{22}(k,j)] - [U - \alpha_{BA}^{21}(k,j)]^2, \quad (15)$$

and

$$R = M_A\omega^2; \quad Q = M_B\omega^2 + (1 - c_B)/\gamma^B. \quad (16)$$

(Note, the unknown U is determined self-consistently for each frequency ω . In equations (14a)–(15), j indicates a cartesian label and atomic species B represents the light atom.)

The weighted particle densities of states are

$$\rho_A = -(2/\pi) \text{Im } \gamma^A; \quad \rho_B = -(2/\pi) \text{Im } \gamma^B, \quad (17)$$

and the total density of states is their sum, i.e.

$$\rho = \rho_A + \rho_B. \quad (18)$$

3. Results

The self-consistent equations (14a)–(14c) have been solved numerically on Temple University CYBER 174. The force constants used were primarily those reported by Rahman *et al* (1976). However, as will become clearer later, our calculations enabled us to compute an improved set of force constants which were then used to calculate our final set of results.

In figure 1(a) we show the phonon partial density of states (PPDS) due to palladium in the alloy PdD_x for $x = 0.63$ –0.9. It is observed that the density of states is hardly affected by such a change in deuterium content. Of course, this fact is largely the result of our model in which the Pd–Pd interaction has been chosen to correspond with that known for the $\text{PdD}_{0.63}$ system, without allowing it to change over the range of concentration studied, i.e. $x = 0.63$ –0.9. Despite this obvious feature, figure 1(a) does contain one useful piece of information: namely, that the deuterium modes seemingly do not mix significantly into the Pd vibrational spectrum for this range of concentration.

In figure 1(b) the deuterium PPDS is plotted for concentrations 63%, 75% and 90%. Besides the obvious increase in weighting, which is linear with deuterium content, we also see the following effect in operation. An increase in D concentration shifts the upper band edge of the deuterium density of states towards higher energies. Additionally, the high-frequency shoulder becomes more prominent and (at the largest D concentration studied, i.e. $x = 0.90$) is seen to be developing additional structure, heralding translational symmetry. This is consistent with the picture that excitations associated with the deuterium sublattice get broadened with increase in vacancies (i.e. with decrease in the deuterium concentration). For the sake of convenient comparison, the total phonon density of states (TPDS) for the PdD_x system is given in figure 1(c).

The lattice dynamics of a single crystal of $\text{PdD}_{0.63}$ has been carefully studied in a series of coherent neutron inelastic scattering experiments by Rowe *et al* (1974). (See also, Bergsma and Goedkop 1961, Chowdhury and Ross 1973.) To make contact with these data, we have used the ISPCA to analyse the phonon dispersion curves for this system. It should, however, be pointed out that the force constants used by Rowe *et al* were obtained by fitting a stoichiometric (i.e. non-random) alloy Born–von Kármán model (valid, say, for PdD) to their experimental results for $\text{PdD}_{0.63}$. (Also see Rahman *et al* (1976), who analysed $\text{PdH}_{0.63}$.) Shortcomings of such fitting procedures include the neglect of shifts in the scattering spectrum to lower frequencies as well as any changes in widths of the resonances, both caused by increase in randomness by the introduction of vacancies into PdD. To improve on such a mean-field-like fitting procedure, we have performed an iterative analysis based on the ISPCA, and recalculated the force constants for the palladium–deuterium system by searching for a ‘best fit’ (see figure 2) to the experimental phonon dispersion curves for $\text{PdD}_{0.63}$. It has turned out that the data are most satisfactorily fitted with essentially the same force constants as used previously (Rowe *et al* 1974, Rahman *et al* 1976) but with the salient difference that the D–D force constants have to be increased by 10% or so. Our results are as follows:

$$\text{D–D} = \begin{pmatrix} \text{first neighbour [110]} \\ 296 & 2075 & 0 \\ 2075 & 296 & 0 \\ 0 & 0 & -339 \end{pmatrix} ; \begin{pmatrix} \text{second neighbour [200]} \\ 2432 & 0 & 0 \\ 0 & -181 & 0 \\ 0 & 0 & -181 \end{pmatrix} . \quad (19)$$

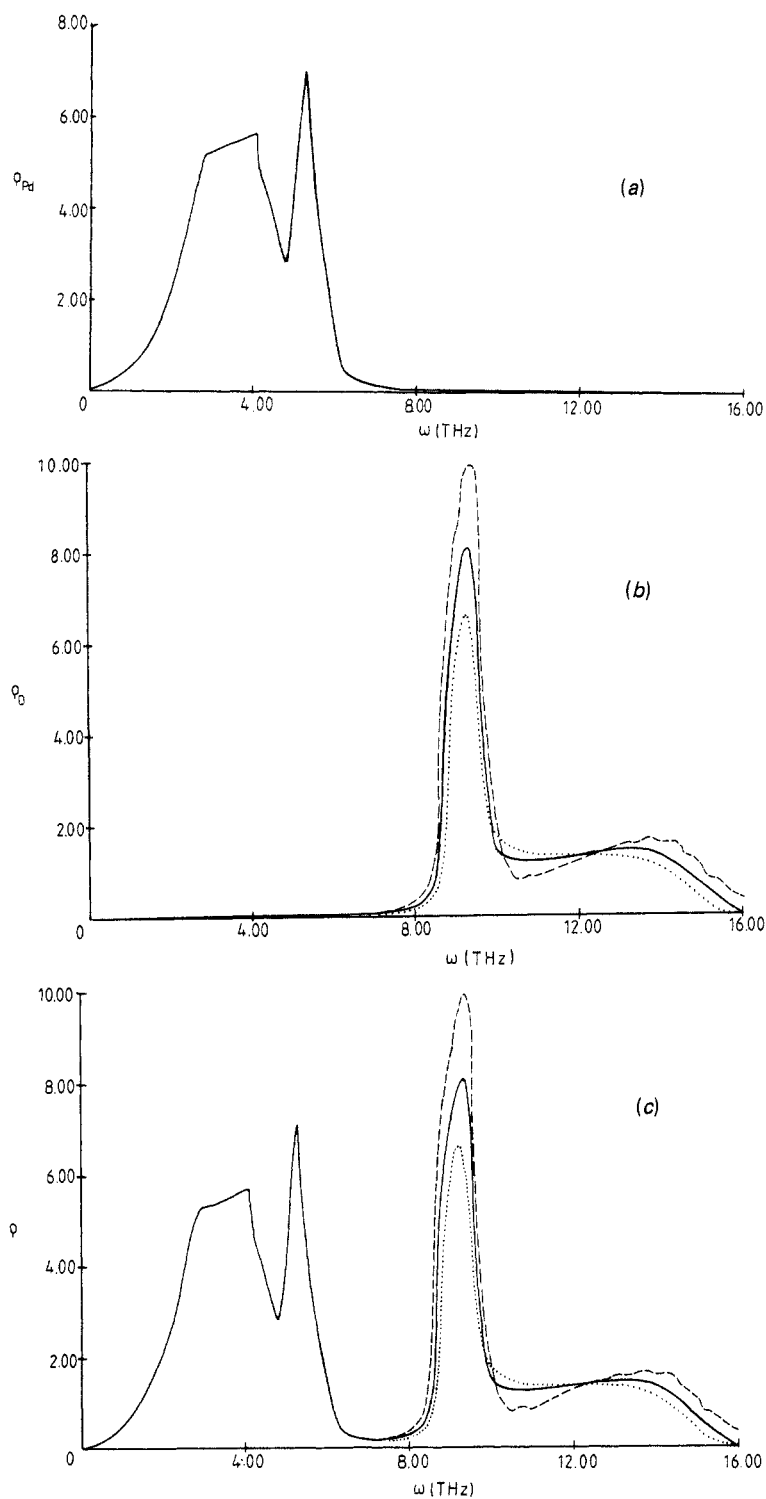


Figure 1. For PdD_x : (a) palladium PPDS for x varying between 0.63 and 0.9; (b) deuterium PPDS and (c) TPDS for $x = 0.63$ (dotted curve), 0.75 (full curve) and 0.9 (broken curve).

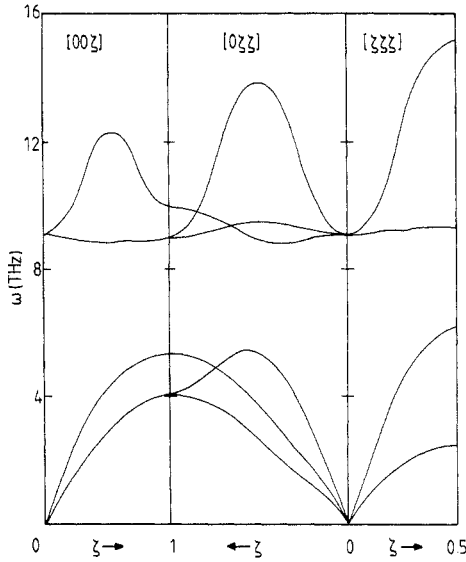


Figure 2. Phonon dispersion curves for $\text{PdD}_{0.63}$. Experimental results of Rowe *et al* (1974) are fitted well by the curves shown obtained by us. Here and in the other figures the wavevector is measured in units of $(2\pi/a)$, where a is the elementary cube edge.

It should be mentioned that since the earlier works (Rowe *et al* 1974, Rahman *et al* 1976), Glinka *et al* (1978) have given an account of a simulation of non-stoichiometric palladium–deuterium system using a variant of the Born–von Kármán method on enlarged cubic cells designed to include some of the dynamical effects of randomness. The present results are in accordance with these authors' observation in that the effective D–D interaction is found to be larger than initially assumed.

To compare with the experimental results for the coherent response, $S(k, \omega)$ for $\text{PdD}_{0.63}$ (Rowe *et al* 1974), we have used the above potentials (which gave the best fit for phonon dispersion curves) to compute the same, i.e.

$$S(k, \omega) = \sum_{\sigma\sigma'} |\bar{b}^\sigma| |\bar{b}^{\sigma'}| \exp[-W_\sigma(k)] \exp[-W_{\sigma'}(k)] (ks_\sigma^i) \times (ks_{\sigma'}^j) \text{Im } G_{ij}^{\sigma\sigma'}(k, \omega). \quad (20)$$

Here the weighted Green functions are given as:

$$G_{ij}^{AA}(k, \omega) = [Q - \alpha_{BB}^{22}(k, j)]/D(k, j) \quad (21a)$$

$$G_{ij}^{BB}(k, \omega) = [R - \alpha_{AA}^{11}(k, j)]/D(k, j) \quad (21b)$$

$$G_{ij}^{AB}(k, \omega) = [\alpha_{AB}^{12}(k, j) - U]/D(k, j) \quad (21c)$$

(compare equations (14a)–(14c)). As usual, $W_\sigma(k)$ denotes the Debye–Waller factor, and $|\bar{b}^\sigma|$ represents the coherent scattering length. Our results for $S(k, \omega)$ are given in figure 3. In order to achieve a direct comparison with experimental results of Rowe *et al* (1974), we show selected phonon groups in figures 4(a)–(c). It is observed that our calculations underestimates the widths slightly. This, unfortunately, is a well known shortcoming of the CPA (Elliott *et al* 1974). However, it does not appear to be too serious in the present case. It should also be mentioned that the present results have not been

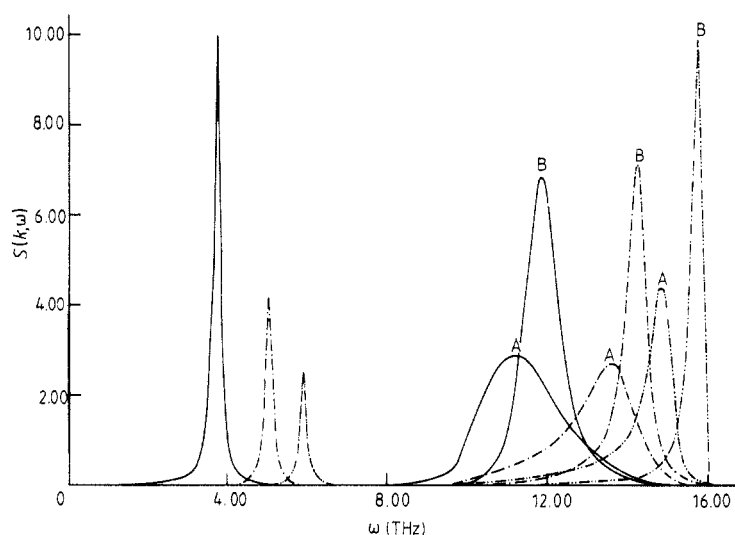


Figure 3. Coherent response function for PdD_x is calculated for wavevectors along the $(\zeta\zeta\zeta)$ direction (L branch) for $x = 0.63$ (curves A) and $x = 0.9$ (curves B). — $\zeta = 0.2$; --- $\zeta = 0.3$; - - - $\zeta = 0.4$; - · - $\zeta = 0.5$.

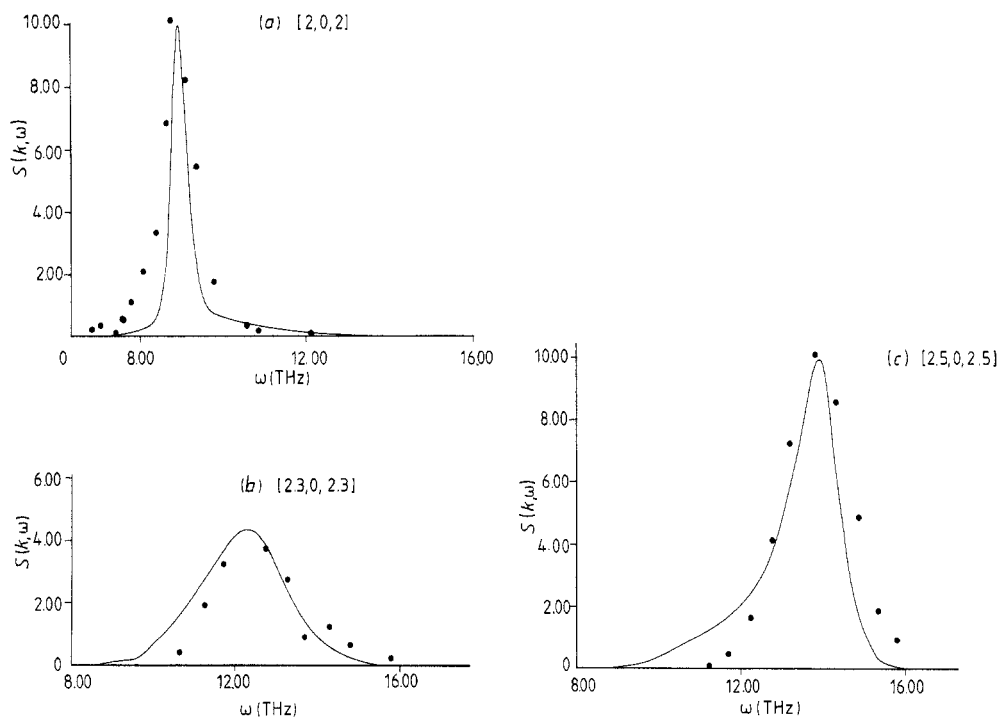


Figure 4. Our results for selected phonon groups in $\text{PdD}_{0.63}$ observed via coherent neutron response are given (full curves). The corresponding experimental results of Rowe *et al* (1974) are shown as full circles. The relevant wavevectors, noted in the figures, are in terms of the ζ notation.

convoluted with the experimental resolutions since the latter were not reported in the literature.

Finally, in figure 5 we present results for the $\text{PdH}_{0.63}$ system. The double differential incoherent scattering cross section is calculated and compared with the corresponding experimental results reported by Rahman *et al* (1976). For this part of the calculation, we have made the usual assumption (Rahman *et al* 1976) of equality between the D–D and the H–H force constants, using our equation (19) for the former. Furthermore, in order to test the usually accepted hypothesis that the Pd–H force constant is approximately 1.2 times that between Pd–D, we have used the Pd–H force constant given by

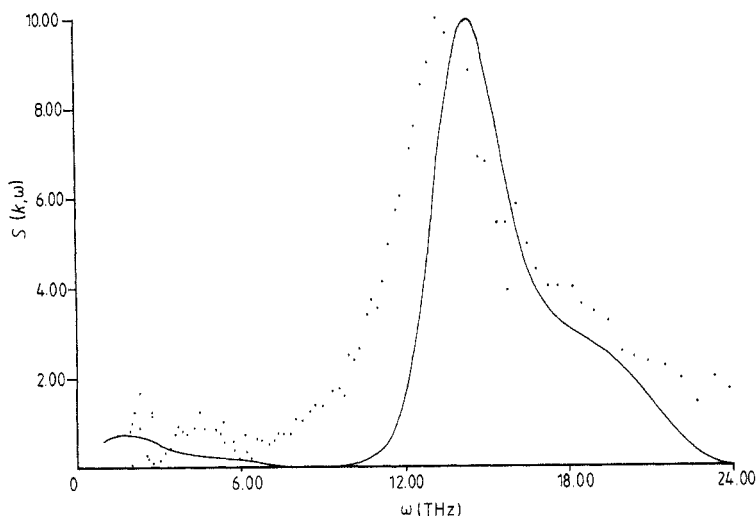


Figure 5. For comparison with the experimental results of Rahman *et al* (1976) on incoherent response from $\text{PdH}_{0.63}$, we have plotted our theoretical results for the double differential scattering cross section (full curve). Experimental results are given as dots.

Rahman *et al* (1976). From figure 5, it is clear that while our calculation reproduces the shape and the width of the incoherent response reasonably well, it is seen to be shifted somewhat towards higher frequencies. This shift, however, is readily corrected if the Pd–H interaction is assumed to be several per cent smaller than that estimated by Rahman *et al*. Accordingly, we conjecture that a conversion factor of 1.1 for the Pd–H/Pd–D force constants is likely to be more accurate than 1.2 usually suggested in the literature.

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