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# Neutron scattering studies of the structure and dynamics of the PdCu–H ordered phase produced under a high hydrogen pressure

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**Abstract.** An atomically ordered PdCuH<sub>≈0.9</sub> hydride was synthesized at 600 K and a hydrogen pressure of 3 GPa. Its metal lattice had a primitive tetragonal cell formed from the initial FCC cell of the disordered PdCu alloy due to ordering of the Pd and Cu atoms into alternate layers perpendicular to the tetragonal *c*-axis. Rietveld refinement of the neutron diffraction pattern of PdCuH<sub>≈0.9</sub> measured at 80 K showed the H atoms to occupy octahedral interstitials within the Pd layers. The inelastic neutron scattering study at 35 K revealed a broad hydrogen optical peak with peculiarities at energy transfers of 79 and 95 meV and of 113 meV which were ascribed to the H vibrations in the Pd–H planes and along the Cu–H chains perpendicular to the planes, respectively. The potential for hydrogen atoms in the PdCuH<sub>≈0.9</sub> ordered phase was thus noticeably different, even in the Pd–H plane, from that in the known hydrides of palladium and palladium alloys. The value of approximately 116 meV was predicted for the local H vibrations in dilute Cu–H solid solutions.

## 1. Introduction

Some years ago, an effect of atomic ordering was observed in the hydrides of Pd–Cu [1] and Pd–Ag [2] disordered alloys produced under high hydrogen pressures and elevated temperatures. A neutron diffraction investigation [3] has shown that the nearly stoichiometric PdAgH<sub>≈0.9</sub> hydride has a primitive tetragonal cell (space group  $P4/mmm$ ) with  $a \approx a_0/\sqrt{2}$ ,  $c \approx a_0$ , where  $a_0$  is the cell parameter of the initial FCC PdAg alloy increased by about 5% due to the hydrogen uptake, and that the structure of the hydride consists of layers  $\cdots\text{Ag-PdH-Ag-PdH}\cdots$  perpendicular to the tetragonal axis with the hydrogens on the octahedral sites within the Pd layers.

The inelastic neutron scattering (INS) study [4] of the ordered PdAgH<sub>0.86</sub> and PdAgH<sub>0.50</sub> hydrides has shown that, due to the specific layered structure, the hydrogen optical phonon group in their spectra was split into two well resolved peaks corresponding to the hydrogen vibrations in the *ab*-plane and along the *c*-axis. This demonstrated for the first time a large difference between the H–Pd and H–Ag interactions and made it possible to estimate the energy (approximately 93 meV) of the local hydrogen vibrations in dilute Ag–H solid solutions never studied experimentally.

A layered ordering of the metal atoms similar to that observed in the PdAg–H hydrides was determined in the Pd<sub>0.6</sub>Cu<sub>0.4</sub>–H hydrides by x-ray diffraction techniques [1, 5]. As copper is a chemical analogue of silver, one could expect the crystal structure of the PdCu–H hydrides to be similar to that of the PdAg–H ones. It seemed thus hopeful that the INS investigation of such hydrides would also permit an isolation of the contributions originated from the H–Pd and, this time, H–Cu interactions and allow an estimation of the latter (Cu–H hydrides are not known; the phonon dynamics of the dilute Cu–H solid solutions has never been investigated).

In the present work, we determined the positions of hydrogen atoms in the crystal structure of PdCuH<sub>≈0.9</sub> hydride by powder neutron diffraction, measured the INS spectrum of the hydride and then fitted it using a conventional Born–von Kármán model.

## 2. Experimental details

The PdCu alloy was melted from Pd (99.98%) and Cu (99.999%) metals in a levitation inductance furnace under an Ar atmosphere and homogenized at 1200 K for 10 h in a vacuum of 10<sup>−4</sup> Torr. Then it was cold rolled into a plate 0.3 mm thick, subjected to stress-relief annealing at 1200 K for 10 min in a vacuum of 10<sup>−4</sup> Torr and quenched in water in order to avoid the atomic ordering to the CsCl-type structure occurring below approximately 780 K [6]. The x-ray examination (100 K, Cu K $\alpha$  radiation) has shown the plate to have a disordered FCC crystal lattice with  $a_0 = 3.759 \pm 0.002$  Å.

An approximately 2 g stack of discs 8 mm in diameter cut out of the PdCu plate, was hydrogenated by a 24 h exposure to a hydrogen atmosphere at  $3 \pm 0.2$  GPa and  $600 \pm 10$  K with subsequent cooling to 100 K. The method is described in more detail elsewhere [7]. At ambient pressure, the PdCuH<sub>x</sub> sample obtained began to lose hydrogen at temperatures above approximately 220 K. The sample was never warmed above 100 K until the measurements were completed. The hydrogen content of the sample determined from the amount of hydrogen liberated during its decomposition at temperatures up to 780 K was  $x = 0.84 \pm 0.05$ . The sample was brittle and we ground it in order to avoid texture effects. Neutron diffraction was measured at 80 K using the time-of-flight diffractometer DN-2 [8] at the IBR-2 reactor, Joint Institute for Nuclear Research, Dubna, Russia. A top-loading cryostat with quartz windows was used in the experiment, and the neutron scattering angle was  $2\theta = 90^\circ$ .

The INS measurements were carried out at 35 K on the time-focused crystal analyser (TFXA) spectrometer [9] at the spallation neutron source, ISIS, Rutherford Appleton Laboratory, UK. Neutrons from a white incident beam scattered by the sample at an angle of  $\approx 135^\circ$  with an energy of 3.8 meV were analysed with a PG crystal and recorded. The spectrometer provided an excellent resolution,  $\Delta\omega/\omega \leq 2\%$  and  $\Delta Q \approx 0.2$  Å<sup>−1</sup>, in the range of energy transfer, studied from 2 to 500 meV. The experiment was done using a top-loading closed-cycle refrigerator with aluminium windows. The data were transformed to  $S(Q, \omega)$  versus energy transfer using standard programs.

## 3. Neutron diffraction

According to the x-ray data, the PdCuH<sub>x</sub> hydride had an atomically ordered tetragonal metal lattice with the cell parameters  $a = 2.794 \pm 0.005$  Å and  $c = 3.678 \pm 0.007$  Å at 100 K.

The neutron diffraction data (figure 1) were taken from the same hydrogenated sample and analysed using the Rietveld profile-refinement program adapted to a time-of-flight

diffractometer [10]. The refinement converged to weighting and profile factors  $R_w = 0.03$  and  $R_p = 0.02$  for a primitive tetragonal structure of PdCuH $_x$ , space group  $P4/mmm$ , with the lattice parameters  $a = 2.792 \pm 0.010 \text{ \AA}$  and  $c = 3.671 \pm 0.013 \text{ \AA}$ , Cu atoms at  $(0, 0, 0)$ , Pd atoms at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , H atoms at  $(0, 0, \frac{1}{2})$  and hydrogen content  $x = 0.95 \pm 0.05$ .

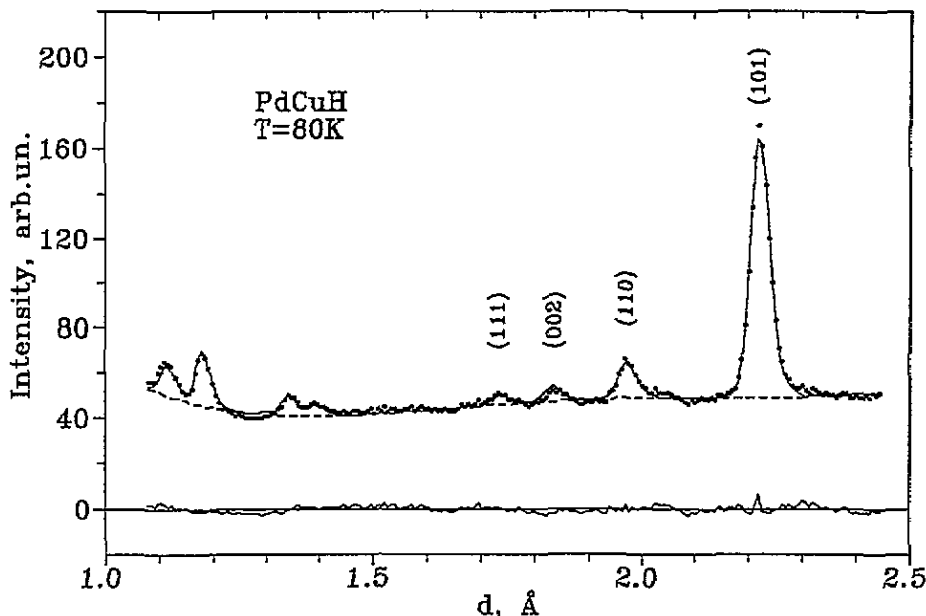


Figure 1. The powder neutron diffraction pattern for PdCuH $_{\approx 0.9}$  at 80 K. Experimental points, fitting and differential curves (solid lines) and estimated incoherent background (dashed line).

Note that, despite the substantial incoherent background from the hydrogen atoms and poor statistics of the experiment, a good convergence of the fit with respect to the hydrogen positioning clearly indicated that the hydrogen atoms occupy only octahedral interstitials within the Pd layers. The crystal structure of the PdCuH $_{\approx 0.9}$  sample was thus similar to that of the PdAgH $_{\approx 0.9}$  hydride [3] with only one exception: the interatomic distance  $r_{\text{Pd-H}} = 1.974 \text{ \AA}$  in PdCuH $_{\approx 0.9}$  was longer than  $r_{\text{Cu-H}} = 1.836 \text{ \AA}$  whereas  $r_{\text{Pd-H}} = 1.999 \text{ \AA}$  in PdAgH $_{\approx 0.9}$  was shorter than  $r_{\text{Ag-H}} = 2.135 \text{ \AA}$ .

## 4. Inelastic neutron scattering

### 4.1. Experimental results

The INS spectrum obtained, figure 2, may be divided into three regions, (i) below 40 meV, where lattice vibrations are mainly determined by motions of the metal atoms, (ii) between 60 and 130 meV, the range of hydrogen optical modes and (iii) above 140 meV, the range of multiphonon neutron scattering.

The statistics at low-energy transfers is insufficient for discussing the details of the lattice part of the spectrum. Note only that it has a larger intensity than in other metal hydrides and stretches up to rather high energies, about 40 meV. For comparison, the high-energy cut-off of the lattice part of the spectra for Pd, Pd-H and PdAg-H is at about 26 meV [11, 12, 4, 13], and for Cu and Cu-Pd alloy it is at about 30 meV [11, 14].

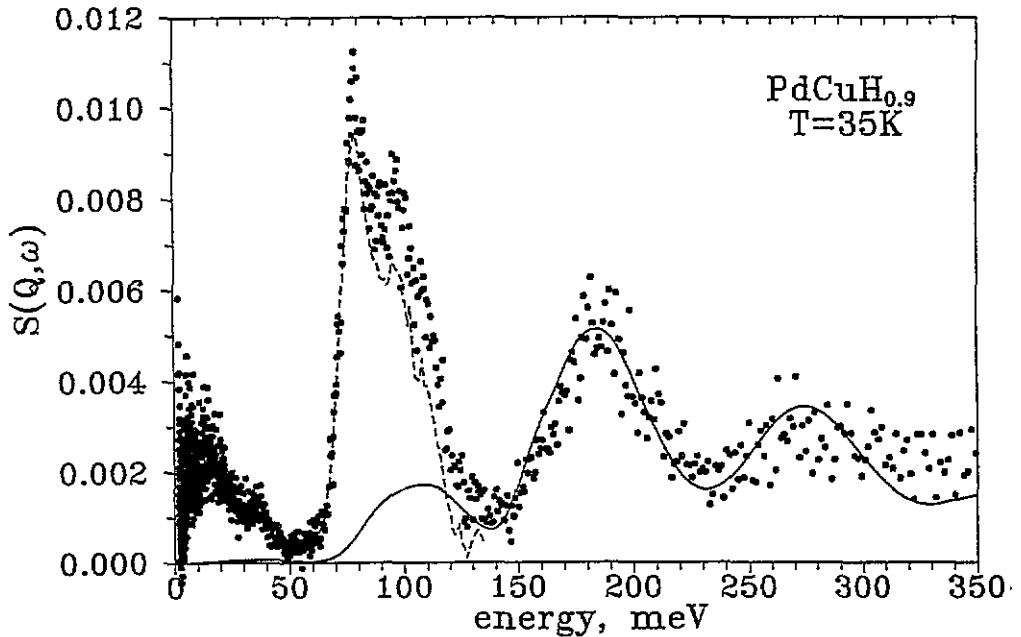


Figure 2. The INS spectrum  $S(Q, \omega)$  for  $\text{PdCuH}_{0.9}$  at 35 K (points). The calculated multiphonon contributions are shown as a solid line. The dashed line is the difference between the experimental data and the calculated multiphonon spectra (the 'one-phonon spectrum').

In order to obtain quantitative information about the INS spectrum  $S(Q, \omega)$  in the range of one- and two-phonon bands, it was treated as a sum of three Gaussians for each band. The parameters of the Gaussians are listed in table 1. For comparison, the hydrogen optical peak in the dilute Pd-H  $\alpha$ -solution ( $r_{\text{Pd-H}} = 1.945 \text{ \AA}$ ) is centred at 69 meV [15], while in  $\beta$ -PdH ( $r_{\text{Pd-H}} = 2.048 \text{ \AA}$ ) it is centred at 56 meV [16, 13], in disordered  $\text{Pd}_3\text{MnH}_{0.03}$  at 74 meV and in ordered  $\text{Pd}_3\text{MnH}_{0.4}$  ( $r_{\text{Pd-H}} = 1.950 \text{ \AA}$ ) at 76 and 83 meV [21]. In the ordered  $\text{PdAgH}_{0.86}$  and  $\text{PdAgH}_{0.50}$ , the hydrogen optical peaks were observed at 63 and 64.4 meV (due to the H vibrations in the Pd-H planes,  $r_{\text{Pd-H}} = 1.999 \text{ \AA}$ ) and at 86 and 90 meV (due to the H vibrations along the Ag-H chains,  $r_{\text{Ag-H}} = 2.135$  and  $2.080 \text{ \AA}$ , respectively) [4].

Table 1. Gaussian peak positions  $\omega_i$  (meV), full widths at half maximum  $\delta_i$  (meV) and peak amplitudes  $H_i$  (arbitrary units) for the hydrogen optical bands of INS spectrum of the  $\text{PdCuH}_{0.9}$  ordered phase.

| Optical bands | One-phonon |         |         | Two-phonon |         |         |
|---------------|------------|---------|---------|------------|---------|---------|
|               | $i = 1$    | $i = 2$ | $i = 3$ | $i = 1$    | $i = 2$ | $i = 3$ |
| $\omega_i$    | 79         | 96      | 113     | 158        | 184     | 212     |
| $\delta_i$    | 11         | 28      | 9       | 10         | 30      | 20      |
| $H_i$         | 0.092      | 0.104   | 0.017   | 0.009      | 0.056   | 0.014   |

Comparing these data with the positions of peculiarities of the hydrogen optical band listed in table 1, we concluded that the first two peaks are associated with the H vibrations

in the Pd-H planes whereas the third peak should mainly originate from the H vibrations along the Cu-H chains perpendicular to the Pd-H and Cu planes. Note, however, that the energy of the optical peak in the PdCuH<sub>≈0.9</sub> ordered phase is the highest among those in the hydrides of palladium and its alloys, and that its value does not agree with the correlation between the energies of such peaks and palladium to hydrogen distances observed in these hydrides. So, the potential for the hydrogen atom in the PdCuH<sub>≈0.9</sub> ordered phase, even in the Pd-H planes, differs noticeably from that in the hydrides of palladium and its alloys.

A  $1/r^\alpha$  dependence, where  $r$  is the metal to hydrogen distance, is often used to estimate variations in the energy of hydrogen vibrations in metal hydrides. The  $\alpha$ -value is usually assumed to be between 1 and 2 [18, 19, 20, 21, 22]. According to the above assignments, the peak at 113 meV in the hydrogen optical band of PdCuH<sub>≈0.9</sub> is due to the Cu-H interaction,  $r_{\text{Cu-H}} = 1.836 \text{ \AA}$ . Because of a close value of  $r_{\text{Cu-H}} = 1.808 \text{ \AA}$  in dilute solid solutions of hydrogen in FCC Cu ( $a = 3.615 \text{ \AA}$  and H on octahedral interstitials), the extrapolated value for the energy of hydrogen optical modes in these solutions lies within  $116 \pm 1 \text{ meV}$  for any choice of  $\alpha$ .

The contributions from the multiphonon neutron scattering (up to four-phonon processes) were calculated in a harmonic isotropic approximation by the multiconvolution of the one-phonon spectrum using an iterative technique [23, 16]. Experimental data in the energy range of the lattice and hydrogen optical phonons, 2–130 meV, were used in the first iterative step as the one-phonon spectrum of hydrogen vibrations. The intensity of the spectrum in the range of lattice vibrations was multiplied by a factor of 0.64 in order to take into account only the contribution from the hydrogen atoms (the factor was estimated from the dynamical calculations for the PdCuH ordered phase described in section 4.2).

In the second and subsequent steps of the multiphonon calculations, the one-phonon spectrum was assumed to be the difference between the experimental one and that resulting from the multiphonon processes. Convergence was reached in three iterations. The results of the calculations are represented in figure 2 by a solid curve for the multiphonon neutron scattering on hydrogen atoms and a dashed curve for the difference between the experimental spectrum and multiphonon contributions (the calculated 'one-phonon spectrum').

As is seen from figure 2, the agreement between the calculated and experimental multiphonon spectra in the range above 140 meV is rather good. In particular, the calculated curve changes its curvature at energies close to those of peculiarities in the experimental spectrum. This allows us to conclude that the behaviour of hydrogen vibrations in the PdCuH<sub>≈0.9</sub> ordered phase is mainly harmonic, and certain discrepancies between the calculation and experiment are probably due to the application of the isotropic approximation for description of the obviously anisotropic object.

#### 4.2. Model calculations of the phonon spectrum

The observed hydrogen optical band (dashed line in figure 2) is rather broad and structured. Judging by the results of the phonon spectra calculations for stoichiometric PdH [12] and non-stoichiometric PdH<sub>0.63</sub> [24], the deviation of the composition of our PdCuH<sub>x</sub> sample from stoichiometry, PdCuH, could lead to much smaller broadening of the optical band. So we made the calculations for a stoichiometric hydride PdCuH, assuming the broadening to be mainly due to a strong H-H interaction and the resulting large dispersion of the optical modes, as is observed in the palladium hydrides.

The calculations were performed in the framework of a conventional Born-von Kármán model using the UNISOFT program [25]. Under the usual assumption that the forces are central, the number of parameters for each atom pair interaction is only two, namely

the longitudinal (L) and transverse (T) force constants. The interaction between the first neighbours for the Pd-Cu, Pd-H and Cu-H pairs, between the first and second neighbours for the Pd-Pd and Cu-Cu pairs, and between first, third and second neighbours for the H-H pairs (at the H-H distances  $a/\sqrt{2}$  and  $a$  in the  $ab$ -plane and  $c$  along the  $c$ -axis, respectively) were taken into account.

The metal-metal force parameters were chosen so as to reproduce the energy cut-off of the lattice vibrations in the measured spectrum around 40 meV and the peculiarities of this spectrum below 10 meV and around 15 and 35 meV; see figure 2. To reduce the number of fitting parameters, we used the same force constants for the Pd-Pd and Cu-Cu interactions (the varying of these constants barely affects the hydrogen optical modes). Thus, the principal adjustable parameters were the force constants for the Pd-H and Cu-H interactions, which determine the average positions of the peaks forming the hydrogen optical band, and those for the H-H interaction, which are responsible for the shape of the band due to dispersion of the optical modes.

The calculated eigenvalues  $\omega_j(q)$  and eigenvectors  $e(i|qj)$  (of atom  $i$ ) of the dynamical matrix corresponding to the phonon state  $qj$  were used to obtain the weighted densities of phonon states according to

$$G_i(\omega) = \frac{1}{3Nm_i} \sum_{j,q} |e(i|qj)|^2 \delta(\omega - \omega_j(q)) \quad (1)$$

where  $m_i$  is the mass of atom  $i$  and the summation extended over  $N = 17576$  points distributed uniformly over a  $q$ -space of the reduced Brillouin zone. To compare the calculated data with the experimental spectrum, we then transformed them via

$$S(Q, \omega) = \sum_i f_i b_i \frac{\hbar Q^2}{6\omega} \exp(-Q^2 \langle u_i^2 \rangle) G_i(\omega) [n(\omega) + 1] \quad (2)$$

where  $b_i$  and  $f_i$  are the neutron scattering cross section and the atomic fraction for atom  $i$ ,  $\langle u_i^2 \rangle$  is a mean square amplitude of vibrations of particle  $i$  (for the hydrogen atoms, a value of  $\langle u_H^2 \rangle = 0.0076 \text{ \AA}^2$  was obtained from the model calculations),  $Q$  is a neutron momentum transfer, and  $n(\omega)$  is the Bose factor.

The calculated  $S(Q, \omega)$  spectrum was fitted to the experimental one by a test-and-trial method. The results of the fit are presented in figure 3; the force constants obtained are listed in table 2.

**Table 2.** The longitudinal (L) and transverse (T) force constants (in  $\text{N m}^{-1}$ ) used for the calculations.

|       | First-neighbour |      | Second-neighbour |      | Third-neighbour |      |
|-------|-----------------|------|------------------|------|-----------------|------|
|       | L               | T    | L                | T    | L               | T    |
| H-H   | 3.4             | -3.0 | 2.5              | -1.5 | 1.4             | -1.0 |
| Pd-H  | 16.7            | 0.0  |                  |      |                 |      |
| Cu-H  | 30.5            | -0.9 |                  |      |                 |      |
| Pd-Pd | 25.0            | -3.4 | -0.7             | 2.0  |                 |      |
| Cu-Cu | 25.0            | -3.4 | -0.7             | 2.0  |                 |      |
| Pd-Cu | 80.0            | -8.0 |                  |      |                 |      |

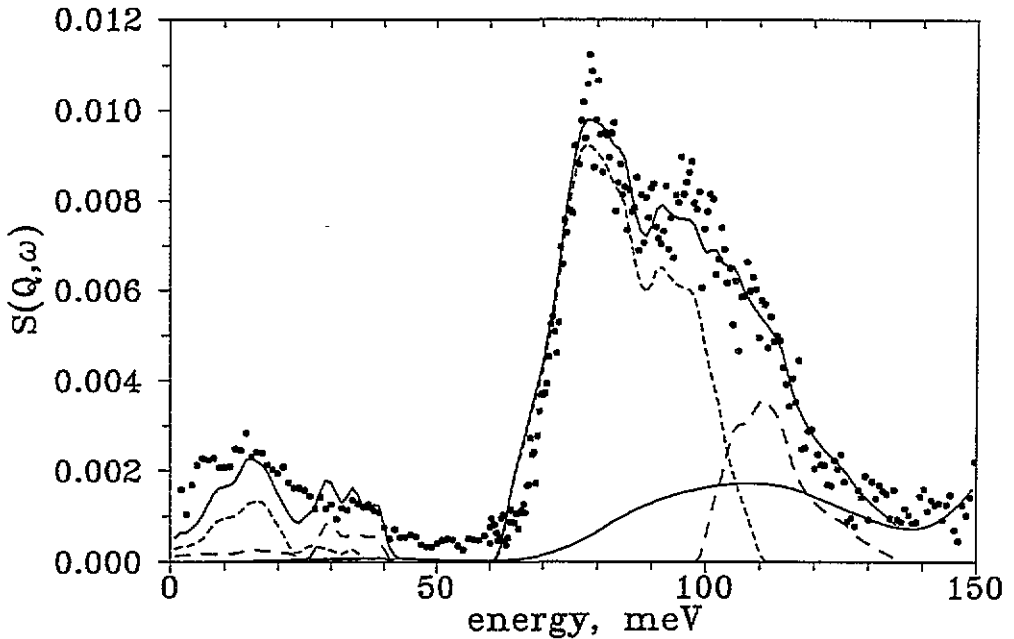


Figure 3. Experimental (points) and calculated (upper solid line)  $S(Q, \omega)$  spectra for PdCuH<sub>0.9</sub>. To obtain the calculated spectrum, the spectrum resulting from the Born-von Kármán model was convoluted with the resolution function for the TFXA spectrometer (a triangle with a width at half maximum of  $\Delta E = 0.02\omega$ ) and then summed with the calculated multiphonon contributions (lower solid line). The contributions to the calculated spectrum from vibrations of H atoms in the *ab*-plane and along the *c*-axis are shown by short- and long-dashed lines.

## 5. Conclusions

Owing to a specific layered crystal structure of the ordered PdCuH<sub>0.9</sub> hydride, it appeared possible for the first time to study the Cu-H interaction. Concluding this paper, we would like to remark on the possible usefulness of the data obtained in attempts to achieve a better understanding of the properties of another copper-containing material, the high-temperature superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>.

Hydrogen is known to affect the superconducting properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> [26] strongly, and many investigations have been undertaken in order to ascertain the nature of the effect. In particular, the vibrational spectra, directly related to the electron coupling, have been thoroughly studied. It was found that the IR absorption spectra exhibit peaks at 104 and 182 meV [27] and INS spectra show a broad band in the energy range from 70 to 130 meV [28, 29, 30, 31] with maxima at about 80, 95, 105 and 125 meV [30, 31].

According to [26], in the unit cell of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> the hydrogens occupy octahedral interstitial sites surrounded by four Ba and two Cu(1) atoms ( $r_{\text{Cu-H}} \approx 1.91 \text{ \AA}$ ) and sites surrounded by four Y and two Cu(2) atoms ( $r_{\text{Cu-H}} \approx 1.94 \text{ \AA}$ ). In the same way as in the case of dilute Cu-H solid solutions considered in section 4.1, one can predict that the hydrogen optical peaks originating from the Cu-H interaction should be positioned at approximately 105 and 101 meV, respectively. It is thus reasonable to expect that among the peaks observed in the experiment, only those at 95 and 105 meV [30, 31] may be due to the Cu-H interaction.



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