Lattice dynamics and phonon line shapes of $Pd_{0.9}Ag_{0.1}D_{0.61}$ at 100 K

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The phonon-dispersion relations in a $Pd_{0.9}Ag_{0.1}D_{0.61}$ crystal have been determined by coherent neutron scattering techniques. In comparison to PdD_x systems, a softening of the acoustic modes by 2% and a hardening of the optic modes by $\approx 4\%$ is observed. Moreover, the optic-phonon groups are considerably broadened because of force-constant disorder when compared to PdD_x. Finally, the present results are discussed in view of the high superconducting transition temperature occurring in the $Pd_{1-y}Ag_yD_x$ system.

I. INTRODUCTION

The palladium-hydrogen system shows some remarkable properties which have attracted considerable interest in recent years, i.e., the high superconducting transition temperature appearing at high hydrogen concentrations,[1] an inverse isotope effect in the critical temperature $T_c(PdH_x) < T_c(PdD_x)$,[2] and furthermore the complicated features of hydrogen ordering at low temperatures.[3] Most of these properties are concentration dependent and have been related to two effects intrinsically connected with the addition of hydrogen to the metal matrix, i.e., the appearance of low-lying optic phonons and the changes of the electronic structure.

The superconductivity in the $PdH_x(D_x)$ system has been ascribed to a BCS coupling induced by the low-lying optic hydrogen vibrations and favored by a rather high density of states of s-type electrons at the Fermi level increasing with hydrogen concentration.[4] The inverse isotope effect in the critical temperature was related to a relative enhancement of the Pd-H force constant due the anharmonicity experimentally observed in the optic-mode frequencies for the two isotopes, i.e., $\omega_{opt}(H) = 1.5\omega_{opt}(D)$ (instead of a factor $\sqrt{2}$ for the harmonic case).[1] Furthermore, the complicated concentration-dependent features of D short-range order at low temperatures were shown to scale with electronic concentration.[5]

In order to investigate separately the contribution of the hydrogen vibrations and of the band-structure characteristics to the onset of superconductivity, experiments on $Pd_{1-y}Ag_yD_x$ (H_x) systems may be appropriate. The substitution of some Pd atoms by Ag induces in PdD_x (H_x) similar changes of the electronic structure—i.e., an increase of s-type electrons—as an increase of hydrogen concentration x. Moreover, in $Pd_{1-y}Ag_yD_x$ (H_x) systems superconducting transition temperatures even higher than those for stoichiometric PdD (H) were found,[6] so that the question arises whether this enhancement of electron-phonon coupling is due to a softening of optic hydrogen vibrations with substitution for Pd of Ag. On the other hand, such a softening does not occur by the increase of hydrogen content x in PdD_x (H_x) systems: Recent neutron scattering investigations have shown the optic-phonon dispersion curves in $PdD_{0.63}$ (Refs. 7 and 8) and $PdD_{0.78}$ (Ref. 9) to be similar, although the lattice constant is different by $\approx 1\%$ and although $PdD_{0.78}$ is superconducting, whereas $PdD_{0.63}$ is not.[1]

In the present paper we report coherent neutron scattering measurements of the phonon dispersion relations in the $Pd_{0.9}Ag_{0.1}D_{0.61}$ system (Sec. III). The phonon density of states is determined via a Born—von Kármán fit and compared to theoretical and earlier experimental results. Finally using the McMillan formula the influence on T_c of the observed changes in the phonon frequencies is estimated (Sec. IV).

II. EXPERIMENTAL

The sample was a cylindrical single crystal of $Pd_{0.9}Ag_{0.1}D_{0.61}$ with the cylindrical axis along the [110] direction. The sample was prepared by loading a $Pd_{0.9}Ag_{0.1}$ single crystal with deuterium from the gas phase under a pressure of 200 bars and finally sealed electrolytically with a copper film.

The measurements were carried out on a conventional triple-axis spectrometer at the Orphée reactor in Saclay. Cu(111) and pyrolitic graphite PG(002) were used as monochromator and analyzer, respectively. The collimations, beginning with the inpile collimator, were 50, 30, 50, 50, minutes of arc. The sample was mounted into a closed-cycle cryostat, and the measurements were done at 100 K. This temperature was chosen to avoid ordering effects of deuterium at lower temperatures, possibly influencing the optic-phonon dispersion.[9] In order to determine accurately the peak positions of the optic phonons, the incoherent background was evaluated by plotting together, for all measured phonons, intensity versus energy curves and taking their lower envelope.

III. RESULTS

The phonon dispersion curves determined in this experiment for the $Pd_{0.9}Ag_{0.1}D_{0.61}$ system at 100 K are shown

in Figs. 1(a) and 1(b), together with the corresponding results for $PdD_{0.63}$ (Refs. 7 and 8) and $PdD_{0.78}$ (Ref. 9) to allow comparison. Whereas no differences between the optic-phonon dispersion of $PdD_{0.63}$ and $PdD_{0.78}$ [as well as $PdD_{0.71}$ (Ref. 10) and $PdD_{0.82}$ (Ref. 11)] have been observed,[9] the substitution for 10 at. % Pd of Ag, as shown in the present experiment, produces observable changes in the dispersion curves.

First, the optic-phonon branches increase by about $\approx 4\%$ in energy. Furthermore the width of the phonon group in $Pd_{0.9}Ag_{0.1}D_{0.61}$ appears to be much larger than that in $PdD_{0.78}$ indicating the presence of a force-constant disorder due to the differences in the Pd-D and Ag-D constants. Some phonon groups for transverse-optic and longitudinal-optic phonons are shown, respectively, in Figs. 2 and 3.

The observed lowering of the acoustic phonon energies [Fig. 1(b)] can be explained by the decrease of the mean

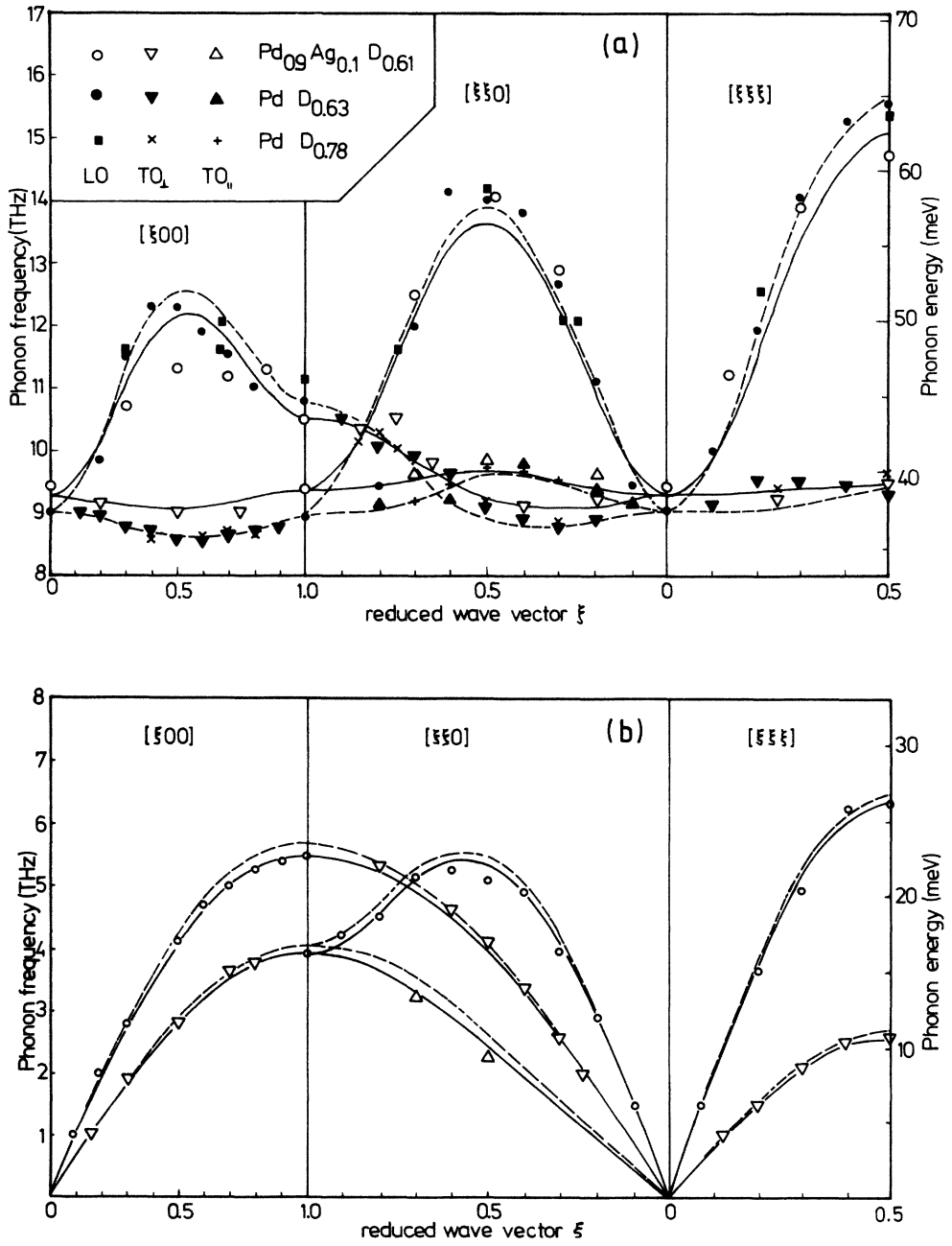

FIG. 1. Dispersion curves of (a) optic and (b) acoustic phonons in $Pd_{0.9}Ag_{0.1}D_{0.61}$ (open symbols) as well as in $PdD_{0.63}$ (Ref. 8) (solid symbols) and $PdD_{0.78}$ (Ref. 9). The solid line represents a Born—von Kármán fit to the dispersion for $Pd_{0.9}Ag_{0.1}D_{0.61}$ and the dashed line for PdD_x ($x=0.63,0.78$).

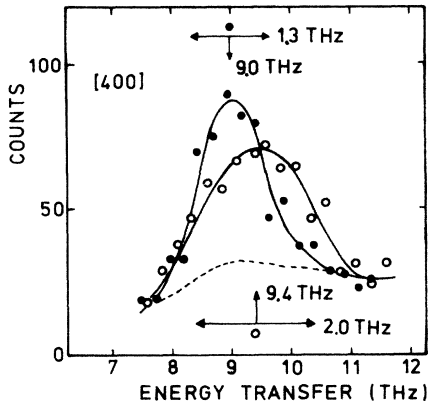

FIG. 2. $q=0$ optic phonon for $PdD_{0.78}$ (solid circles) and $Pd_{0.9}Ag_{0.1}D_{0.61}$ (open circles). The dashed line represents the incoherent background, and the arrows indicate the position and the full width at half maximum of the peaks.

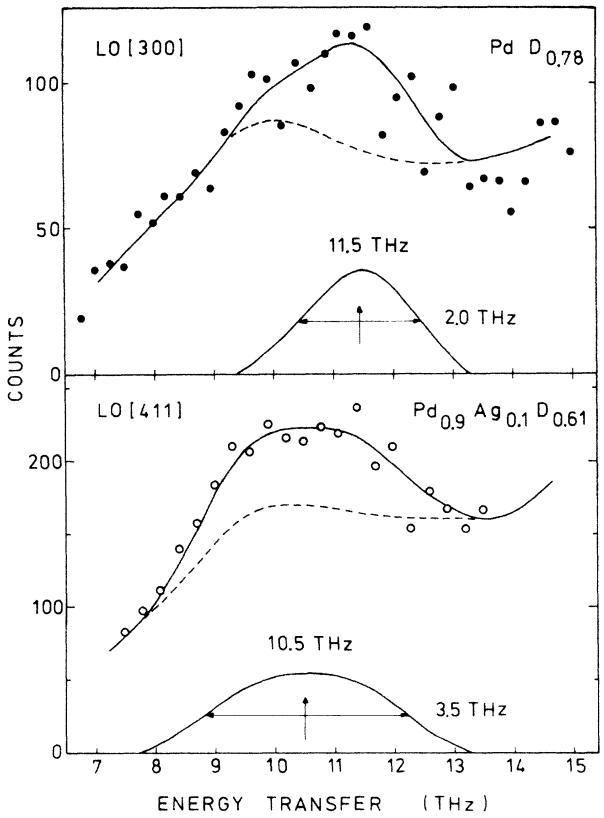

FIG. 3. LO[100] phonon for $PdD_{0.78}$ (solid circles) and $Pd_{0.9}Ag_{0.1}D_{0.61}$ (open circles). The dashed line represents the incoherent background for each measurement. The difference between curve and background is also drawn, and the position and width of the maximum is indicated.

metal-metal force constant due to the partial substitution of Pd and Ag. Effectively the Debye temperatures of Pd and Ag are 274 and 225 K, respectively,[12] so that a linear interpolation gives a decrease of Debye temperature from Pd to $Pd_{0.9}Ag_{0.1}$ by $\approx 1.8\%$, which is in good agreement with the observed softening of the acoustic branches. The hardening of the transverse-optic-phonon branches [Fig. 1(a)], on the other hand, indicates that the partial substitution of Pd-D by Ag-D leads to an effective increase of the mean metal-deuterium force constant, the differences between Pd-D and Ag-D interaction being also responsible for the considerable broadening of the optic-phonon groups (Figs. 2 and 3). In addition, the dispersion of the

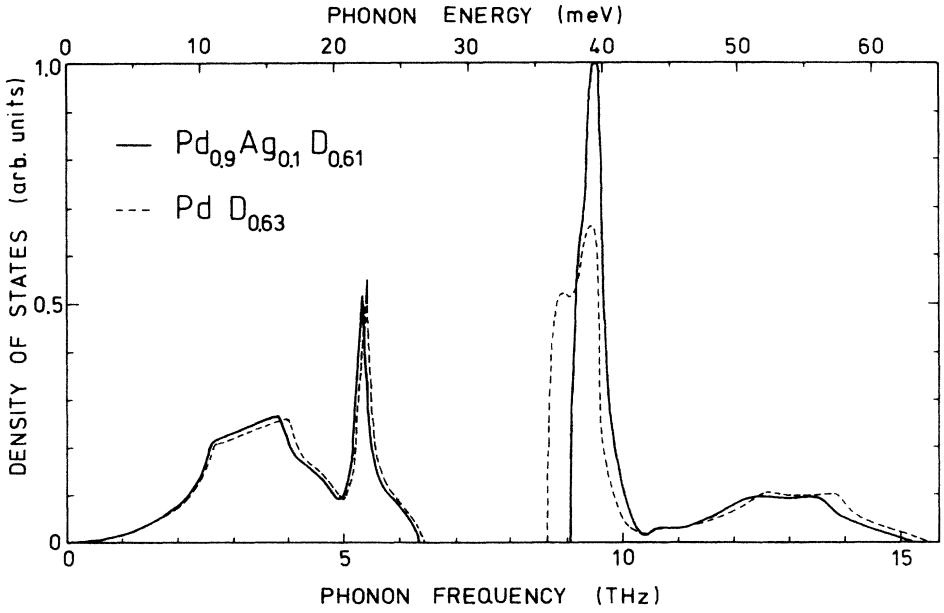

FIG. 4. Phonon density of states of $Pd_{0.9}Ag_{0.1}D_{0.61}$ (solid line) computed from the force constants obtained by a 12 parameter Born–von Kármán fit to the dispersion curve (Fig. 1). The dashed line is the phonon DOS from Ref. 7 for $PdD_{0.63}$ nearly identical with that of $PdD_{0.78}$ (Ref. 9).

longitudinal branches seem reduced, especially in the [100] direction [Fig. 1(a)] which may indicate a somewhat lower D-D interaction in $Pd_{0.9}Ag_{0.1}D_x$ than in PdD_x.

These main features are reproduced by a Born–von Kármán fit (12 parameters) to the dispersion curves of $PdD_{0.78}$ (from Ref. 9) and of $Pd_{0.9}Ag_{0.1}D_{0.61}$ (present experiment), which is shown in Figs. 1(a) and 1(b) by broken and solid line, respectively. The obtained force constants were used to compute the density of states (DOS) in the case of $Pd_{0.9}Ag_{0.1}D_{0.61}$ which is drawn in Fig. 4 together with the DOS for $PdD_{0.63}$.[7] Besides the weak softening of the acoustic phonons, the main characteristic is the shift of the sharp peak in the optical part of the DOS to somewhat higher energies (by $\approx 4\%$). The increase in height of this peak reflects the slightly lower dispersion of the transverse optic branches in $Pd_{0.9}Ag_{0.1}D_{0.61}$. These features are in qualitative agreement with DOS calculations by Sansores *et al.*[13] assuming force constant disorder due to the difference in the Pd-D and Ag-D interaction, which is supported experimentally by the broadening of optic phonons (Figs. 3 and 4).

The present results contrast, however, with early incoherent neutron scattering measurements on $Pd_{1-y}Ag_yH_x$ by Chowdhury and Ross[14] who did not report any significant change in the peak position of the time-of-flight spectra, when compared to PdH_x. The present results, are however, supported by coherent neutron scattering measurements of the whole phonon dispersion curve, whereas for the early time-of-flight measurements poor resolution could have masked the frequency shifts.

IV. SUPERCONDUCTIVITY

In this section we will briefly discuss the consequences of the present results on the onset of superconductivity in palladium-hydrogen systems. Starting with the McMillan's approximation, we use the electron-phonon coupling constant λ which can be written in the case of compounds with large mass difference between the atoms as a sum

$$\lambda = \lambda_{ac} + \lambda_{opt} ,$$

where λ_{ac} and λ_{opt} describe the coupling with the acoustic and the optic phonons, respectively.

$$\lambda_{ac} = \frac{\eta_{ac}}{M_M \bar{\omega}^2_{ac}}, \quad \lambda_{opt} = \frac{\eta_{opt}}{M_D \bar{\omega}^2_{opt}} ,$$

where M_M and M_D are the masses of the metal and deuterium atom, respectively, and $\bar{\omega}^2_{ac}$ and $\bar{\omega}^2_{opt}$ the mean-square values of the acoustic and optic phonon frequencies. T_c can then be calculated with the McMillan formula

$$T_c = \frac{\langle \omega \rangle}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - 0.13(1+0.62\lambda)} \right] , \tag{1}$$

where $\langle \omega \rangle$ is some mean phonon frequency. In a recent band-structure calculation Papaconstantopoulos *et al.*[15] have determined η_{ac} and η_{opt} in function of hydrogen concentration in $Pd_{1-y}Ag_yD_x$ (H_x). They found a stronger coupling for higher hydrogen concentrations x as well as for higher silver content y induced by an enhancement at the hydrogen site of the s-like electron density of states at the Fermi level. They further calculate T_c with formula (1) with the following assumptions.

(a) $\bar{\omega}^2_{ac}$ and $\bar{\omega}^2_{opt}$ are both independent of hydrogen concentration x.

(b) $\bar{\omega}^2_{ac}$ is estimated by rescaling its value in PdD_x using the Debye temperatures of Pd and Ag.

(c) $\bar{\omega}^2_{opt}$ is independent of silver content y.

Hypothesis (a) is quite well verified in PdD_x for $0.63 < x < 0.8$ (Refs. 7–11) and hypothesis (b) is shown by the present experiment on $Pd_{0.9}Ag_{0.1}D_{0.61}$ to be a reasonable assumption (Sec. III), whereas hypothesis (c) is not confirmed by the present experiment (Sec. III).

We have therefore tried to estimate how the T_c values obtained by Papaconstantopoulos *et al.*[15] would be shifted when small variations of the phonon dispersion curve $\epsilon_{ac} = \Delta\omega_{ac}/\omega_{ac}$ and $\epsilon_{opt} = \Delta\omega_{opt}/\omega_{opt}$ are taken into account. Whereas in the original theory $\epsilon_{opt} = \epsilon_{ac} - \epsilon^0_{ac} = 0$ ($\epsilon^0_{ac} = y[\Theta_D(\mathrm{Ag})/\Theta_D(\mathrm{Pd}) - 1]$, Θ_D is the Debye temperature), we have estimated the influence of ϵ_{opt} and ϵ_{ac} by differentiating the McMillan formula (1) in the form

$$\Delta T_c / T_c = \Gamma_{opt}\epsilon_{opt} + \Gamma_{ac}(\epsilon_{ac} - \epsilon^0_{ac}) , \tag{2}$$

where T_c, Γ_{ac}, and Γ_{opt} are computed using the original parameters of Ref. 15. T_c, Γ_{ac}, and Γ_{opt} appear essentially as functions of λ_{opt} (as λ_{ac} is nearly constant) and the results are shown in Fig. 5.

The dominant contribution to $\Delta T_c/T_c$ arises from optical phonons because Γ_{ac} is small (Fig. 5) and also $\epsilon_{ac} - \epsilon^0_{ac}$ has been shown to be small in the present experiment (Sec. III). We therefore obtain that $\Delta T_c/T_c \sim \Gamma_{opt}\epsilon_{opt}$, where $\Gamma_{opt} \approx -3$ for the highest T_c values ($T_c \sim 15$ K) observed in the palladium-silver-deuterium system. In Table I are listed some numerical values calculated with the formulas given in Ref. 15. An increase in the optical phonons as in the present experiment with $y = 0.1$ ($\epsilon_{opt} \approx 4\%$) would therefore mean a reduction of the calculated T_c by 12%, when compared to the estimate by Papaconstantopoulos *et al.*[15] As λ_{opt}, and therefore T_c, are strongly dependent on the exact deuterium concentration in the sample, the

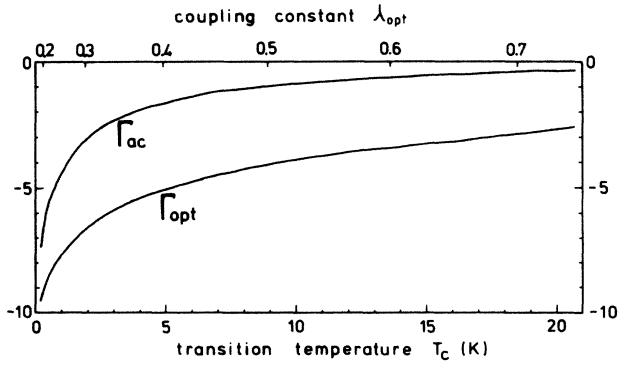

FIG. 5. Γ_{ac} and Γ_{opt} as defined by Eq. (2), where T_c is calculated using the McMillan formula [Eq. (1)]. The numerical values for the constants entering in these equations are taken from Ref. 11. In particular λ_{ac} is nearly constant and $\lambda_{ac} \sim 0.18$.

TABLE I. T_c values for $Pd_{1-y}Ag_yD_x$.

y	Measured T_c (Ref. 6)	Calculated T_c after Ref. 15		
0	9 K	8.9[a]		
15%	14 K	13.8[a]	12.0[b]	11.0[c]
30%	15 K	15.9[a]	13.9[b]	9.9[c]
50%	not superconducting	12.4[a]	10.7[b]	3.7[c]

[a] $\epsilon_{opt}=0$.
[b] $\epsilon_{opt}=4\%$.
[c] A linear increase of ϵ_{opt} with y is assumed so that for $y=10\%$, $\epsilon_{opt}=4\%$. ϵ_{opt} is as defined in the text.

agreement between the experimental and calculated T_c may however be restored, when a somewhat higher deuterium concentration as in Ref. 15 is assumed for the samples used in the T_c measurements[6] (where the D concentration could only be crudely estimated). In addition, a further hardening of optical phonons when the Ag content y increases would lead to the break down of superconductivity for some values of y, which is indeed experimentally observed for $y>0.4$ (Ref. 6) and could not be explained by band-structure arguments.[15]

V. CONCLUSION

The phonon dispersion and phonon line shapes of $Pd_{0.9}Ag_{0.1}D_x$ have been measured by means of coherent neutron scattering and compared to the results for PdD_x. One observes a softening of the acoustic branches by about $\sim 2\%$ which may be described by rescaling the phonon frequencies from Pd to $Pd_{0.9}Ag_{0.1}$ using the Debye temperatures of Pd and Ag.

The optical-phonon groups are considerably broadened when compared to PdD_x and the frequencies of the transverse-optic branches are increased by $\approx 4\%$. This may qualitatively be understood by the force-constant disorder due to the difference in Pd-D and Ag-D interaction.

The hardening of transverse-optic phonons induces a shift of the maximum of the phonon density of states to higher frequencies. This should decrease the electron-phonon coupling and therefore reduce the superconducting transition temperature. As this hardening of optic phonons is not included in the usual theories for superconductivity in $Pd_{1-y}Ag_yD_x$, we have estimated its effect on T_c using the theoretical framework by Papaconstantopoulos *et al.*[15] For the observed increase of transverse-optic-phonon frequencies by only $\sim 4\%$ in $Pd_{0.9}Ag_{0.1}D_{0.61}$ we estimate a decrease of the calculated T_c of already 12%, so that an eventual further hardening of optic phonons for higher silver contents could possible lead to the breakdown of superconductivity observed for a silver concentration $y>0.4$.[6]

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