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Neutron spectroscopy of $ReH_{0.09}$

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A powder and a single-crystalline sample of a solid hydrogen solution in hcp rhenium with an atomic ratio of H/Re$=$0.09 were synthesized under a high pressure of gaseous hydrogen and studied by inelastic neutron scattering in the range of energy transfers from 25 to 380 meV. The fundamental band of optical hydrogen vibrations was found to be split into two sharp peaks centered at 100 and 130 meV. The peaks have an intensity ratio of about 1:2 and the corresponding vibrations are polarized along the *c* axis and in the basal plane of the crystal lattice, respectively.

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I. INTRODUCTION

Rhenium is a hcp 5*d* metal of group VII and it belongs to a rather large variety of group VI–VIII transition metals that form hydrides with close-packed metal lattices of fcc, hcp, or *double* hcp structure, in which hydrogen occupies octahedral interstitial positions (see papers in Refs. 1–3 for references). The lattice dynamics of hydrides of Cr, Mn, Fe, Co, Ni, Mo, and Pd have been studied by inelastic neutron scattering (INS) (see papers in Refs. 3 and 4 and references therein). The fundamental optical hydrogen band in all those hydrides was found to look similar and to consist of a sharp peak with a large shoulder extending towards higher energies. Based on results for palladium hydride,[5] the sharp peak could be attributed to nondispersive transverse phonon modes and the shoulder to longitudinal modes exhibiting significant dispersion due to long-range repulsive H-H interaction.

The present paper reports on the results of an INS investigation of the spectrum of optical vibrations of hydrogen in hcp rhenium, which exhibits a different behavior. The INS spectrum of a $ReH_{0.09}$ powder sample was measured at two temperatures, 5 and 90 K, in order to study the effect of temperature. A single-crystalline $ReH_{0.09}$ sample was studied by INS to determine the polarization of the hydrogen vibrations. It was measured at 5 K in two orientations, with the *c*-axis parallel and at an angle of 63° to the direction of neutron momentum transfer. Additionally, the crystal structure of the $ReH_{0.09}$ powder sample was examined by neutron diffraction at 90 K.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The starting materials were Re metal powder of 99.99 wt. % purity and a single crystal of Re with an electric resistance ratio $R_{300\ \mathrm{K}}/R_{4.2\ \mathrm{K}} \approx 150$. The single-crystalline sample was a disc of 0.5 mm thickness, cut parallel to the basal plane of the hcp metal lattice.

Similar to many other *d* metals of the groups VI–VIII,[6] rhenium absorbs a considerable amount of hydrogen at high hydrogen pressures and elevated temperatures, and the resultant phases can be removed from the high-pressure cell and studied at ambient pressure in a metastable state if cooled to a lower temperature beforehand. The equilibrium hydrogen solubility in hcp rhenium at temperatures from 170 to 350 °C has earlier been found to increase monotonically with hydrogen pressure, reaching an H-to-metal atomic ratio of $x \approx 0.22$ at 9 GPa.[7,8] At ambient pressure, the quenched metastable ReH_x samples begin to lose hydrogen when warmed above 0 °C. In the present work, a 5.4 g $ReH_{0.09}$ powder sample and a 0.79 g single-crystalline $ReH_{0.09}$ sample were prepared by a 24 h exposure of rhenium to an H_2 pressure of 6 GPa at 325 °C and subsequent cooling to 150 K in the high-pressure cell. The hydrogenation method is described elsewhere.[6] When not in use, the quenched samples were stored in liquid nitrogen; in the course of the measurements they were never warmed above 120 K. The hydrogen content $x = 0.094$ of the samples was determined by hot extraction into a calibrated volume at temperatures up to 500 °C using 0.12 g of the powder sample.

The INS spectra of both $ReH_{0.09}$ samples were measured in the range of energy transfer $25\ \mathrm{meV} \leqslant \omega \leqslant 380\ \mathrm{meV}$ with a resolution of $\Delta\omega/\omega \approx 5.5$ to 8% using the beryllium filter spectrometer IN1 installed at the hot source of the high-flux reactor at the Institute Laue-Langevin in Grenoble. The scattering angle was fixed at 25° and a Cu(220) monochromator was used to scan the energy of the incoming neutrons. The ω value was calculated by subtracting 3 meV, the mean energy of neutrons transmitted through the cooled Be filter, from the incident neutron energy. Due to this small final energy of the recorded neutrons, the deviation of the momentum transfer vector, $\boldsymbol{Q}$, from the direction of the incident neutron beam was only a few degrees for $\omega > 90\ \mathrm{meV}$, the range of optical

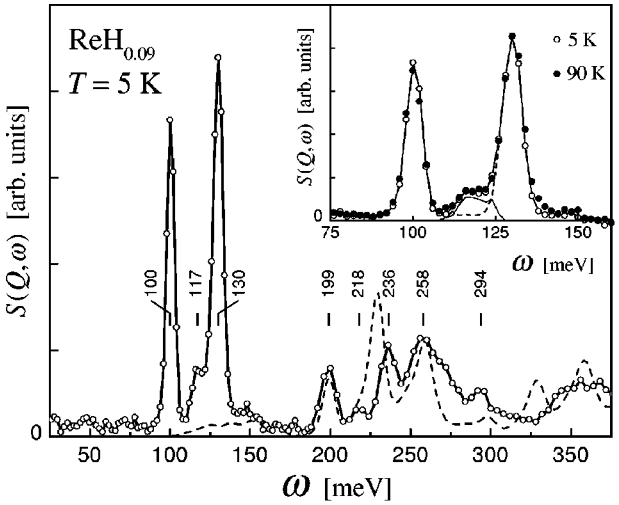

FIG. 1. The dynamical structure factor $S(\mathbf{Q},\omega)$ of $ReH_{0.09}$ powder at 5 K as a function of the energy loss ω of the inelastically scattered neutrons. The dashed line represents the multiphonon contribution calculated in an isotropic harmonic approximation. The inset shows the "one-phonon" spectra of $ReH_{0.09}$ powder at 5 and 90 K obtained by subtracting the calculated multiphonon contributions from the experimental INS spectra.

hydrogen vibrations in $ReH_{0.09}$. The samples were enclosed in a flat thin aluminum container framed with a Cd mask. Background spectra from an empty container were measured separately under the same conditions and then subtracted from the raw INS spectra of the samples.

A neutron diffraction pattern of the $ReH_{0.09}$ powder sample was measured at 90 K with neutrons of a wavelength $\lambda = 1.286$ Å using the D1B diffractometer at ILL, Grenoble. The diffractometer was equipped with a position sensitive detector, covering 80° in 2ϑ with 400 cells of 0.2° width. The sample was placed in a cylindrical, thin-walled vanadium can. The background was determined in a separate empty-can measurement and subtracted from the measured diffraction pattern.

III. RESULTS AND DISCUSSION

A. Inelastic neutron scattering from $ReH_{0.09}$ powder

The $ReH_{0.09}$ powder sample was distributed in a 0.3 mm thick layer between the parallel walls of the aluminum container, which was aligned with its flat side perpendicular to the incoming neutron beam. In this geometry and for the incident neutron energies relevant to the experiment (100 to 300 meV; Fig. 1), the total neutron scattering from the sample was less than 4% and the neutron absorption varied from 4.7 to 2.7%. Effects caused by multiple neutron scattering and neutron absorption were therefore neglected in the analysis of the experimental INS spectra.

The INS spectra of the $ReH_{0.09}$ powder sample measured at 5 and 90 K nearly coincide. The spectrum measured at 5 K is shown in Fig. 1. Two well resolved INS peaks in this spectrum are located within the energy range of 60 to 170 meV, where the fundamental optical hydrogen band for the hydrides of the group VI–VIII transition metals studied so far is typically found. It therefore seems reasonable to attribute these two peaks to the fundamental optical hydrogen band of $ReH_{0.09}$. The first narrow peak is centered at $\omega_1 = 100$ meV, the second peak has a maximum at $\omega_2 = 130$ meV and a shoulder around $\omega_{sh} = 117$ meV. Combinations of these three energies can account for the positions of the peaks observed at higher energy transfers: The peaks at 199 meV$\approx 2\omega_1$ and at 294 meV$\approx 3\omega_1$ can be considered as the second and third harmonics of the peak at ω_1; the peak at 258 meV$\approx 2\omega_2$ as the second harmonic of the peak at ω_2. The peak at 236 meV and the small peak at 218 meV can be attributed to the combinations $\omega_1 + \omega_2 = 230$ meV and $\omega_1 + \omega_{sh} = 217$ meV, respectively. The broad peak at energy transfers higher than 330 meV is presumably due to the overlapping excited states with energies close to $2\omega_1 + \omega_2 = 330$ meV and $\omega_1 + 2\omega_2 = 360$ meV.

In view of the negligibly small intensity of multiple neutron scattering due to the small thickness and low hydrogen content of the $ReH_{0.09}$ sample, the occurrence of the peak at 236 meV$\approx \omega_1 + \omega_2$ shows that the peaks at $\omega_1 = 100$ meV and $\omega_2 = 130$ meV in the fundamental optical hydrogen band are due to neutron scattering from hydrogen atoms occupying crystallographically equivalent positions. If these peaks were due to neutron scattering from hydrogen atoms on inequivalent sites characterized by the excitation energies ω_1 and ω_2, the second H optical band would exhibit only two peaks at around $2\omega_1$ and $2\omega_2$. A mixed-type excitation at $\omega \approx \omega_1 + \omega_2$ can arise only when the individual hydrogen atoms have vibrational excited states with ω_1 and ω_2. The conclusion that hydrogen occupies only a single interstitial site in $ReH_{0.09}$ is valid for $T = 5$ K as well as for $T = 90$ K, because the INS spectra measured at these two temperatures are nearly identical. It also agrees with the result of a neutron diffraction investigation[9] showing that at 90 K hydrogen occupies only octahedral interstices in the hcp metal lattice of $ReH_{0.2}$.

To visualize the degree of anharmonicity of the optical vibrations of hydrogen in $ReH_{0.09}$, the INS spectrum at energies above the fundamental band was calculated in an isotropic harmonic approximation including processes involving up to four phonons. The calculation was done by an iterative technique[10] using a multiconvolution of the one-phonon spectrum of lattice and optical phonons in the energy region $\omega < 140$ meV. Since the low-energy lattice part of the spectrum has not been measured yet, it was calculated in the Debye approximation using the Debye temperature $T_D = 415$ K of pure rhenium. The use of this rough approximation should not noticeably affect the results of the calculation because the ratio of the integrated intensities of the lattice and fundamental optical band of hydrogen is very small—of the order of the ratio of 1:186 of the H and Re atomic masses—and because the intensity of multiphonon scattering involving lattice phonons is not very high due to the low temperature of the sample. The mean-square displacement of the hydrogen atoms, $\langle u^2 \rangle = 0.019$ Å^2, resulting from the calculation seems reasonable.

The calculated "multiphonon" spectrum is shown in Fig. 1 by the dashed line. As one can see, it satisfactorily reproduces the positions and intensities of the optical H peaks near $2\omega_1$, $3\omega_1$, and $2\omega_2$, which can therefore be considered as harmonics of the corresponding fundamental peaks, inheriting their polarizations. At the same time, the convolution calculation for ω_1 with ω_{sh} and ω_2 produces a broad peak with a maximum slightly below 230 meV, while the experiment revealed two peaks at 218 and 236 meV. We attribute this difference to considerable anharmonic effects pertaining to excitations polarized differently than the fundamental modes. This observed deviation from harmonic behavior in the INS spectrum of $ReH_{0.09}$ is much stronger than in the powder INS spectra of hydrides of the group VI–VIII transition metals studied previously.[3]

In the range of the fundamental optical band, the contribution from multiphonon scattering to the total scattering intensity is not large and it does not change the specific features of the spectrum. The inset of Fig. 1 shows the practically coinciding "one-phonon" spectra of $ReH_{0.09}$ at 5 and 90 K obtained by subtracting the calculated "multiphonon" spectra from the experimental ones. The peaks at 100 and 130 meV have full widths at half maximum of about 6 and 7 meV, respectively, equal to the resolution of the spectrometer at these energy transfers. The peaks can therefore be attributed to nearly nondispersive modes of optical hydrogen vibrations. To outline the profile of the intensity distribution that forms the low-energy shoulder of the second peak, the mirror image of its high-energy side (shown as dashed line in the inset) was subtracted from the experimental data. The integrated intensity of the resulting feature shown by the thin solid line amounts to about 20% of the intensity of the second peak. The full width at half maximum of this feature is about 12 meV, thus considerably exceeding the spectrometer resolution. The feature therefore cannot be ascribed to another nondispersive optical mode and must rather originate either from the dispersion caused by H-H interactions or from the nonharmonic shape of the hydrogen potential well along certain directions in the crystal structure of $ReH_{0.09}$.

In the "one-phonon" spectrum shown in the inset of Fig. 1, the ratio of the integrated intensities of the first and the second fundamental peak taken together with its low-energy shoulder is about 1:1.65. When the "one-phonon" spectrum is transformed to the density of vibrational states by correcting for the Debye-Waller factor, $\exp(-\boldsymbol{Q}^2\langle u^2\rangle)$ with $\langle u^2\rangle = 0.019$ Å^2, this intensity ratio becomes 1:2.15. In view of the large uncertainty in the value of $\langle u^2\rangle$ obtained in the isotropic harmonic approximation, which could not reproduce the experimental INS spectrum well enough, this ratio seems actually very close to 1:2.

Assuming a random distribution of H atoms over the octahedral interstices in the hcp metal lattice of $ReH_{0.09}$, the small hydrogen content of the solution should result in only weak H-H interactions, so that in a first approximation the hydrogen atoms can be considered as independent three-dimensional local oscillators. In this picture, the number and intensity ratio of the peaks in the fundamental optical band of $ReH_{0.09}$ finds a straightforward explanation by attributing the peak at $\omega \approx 100$ meV to a vibrational mode of hydrogen atoms polarized along the c axis of the hexagonal crystal structure. The peak at $\omega \approx 130$ meV will then result from two degenerate modes polarized perpendicular to this axis, i.e., in the hexagonal basal plane. The INS measurements on the single-crystalline $ReH_{0.09}$ sample confirmed the suggested polarization of the fundamental peaks.

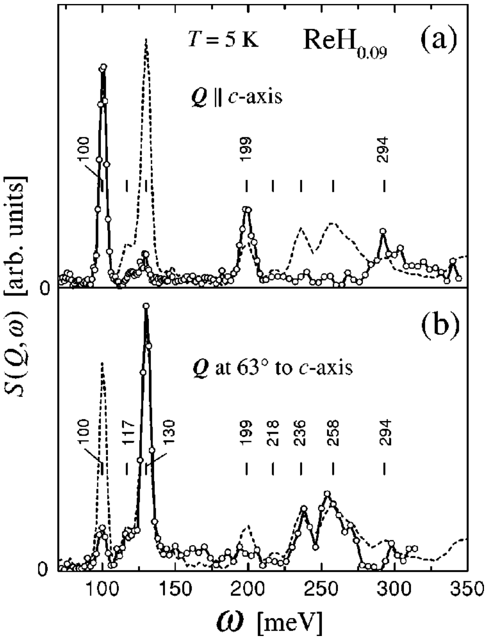

FIG. 2. The INS spectra of a $ReH_{0.09}$ single crystal measured at 5 K in two orientations, with the c-axis parallel the vector $\boldsymbol{Q}$ of neutron momentum transfer (a) and at an angle of 63° to the direction of $\boldsymbol{Q}$ (b). The dashed lines represent the INS spectrum of $ReH_{0.09}$ powder at 5 K shown in Fig. 1.

B. Inelastic neutron scattering from $ReH_{0.09}$ single crystal

The $ReH_{0.09}$ single-crystal was mounted in the cryostat with its crystallographic a axis directed vertically. The crystal was first measured with the c-axis parallel to the vector $\boldsymbol{Q}$ of neutron momentum transfer. Since the crystal had the shape of a disc cut along the basal plane of the hcp metal lattice, its surface was approximately perpendicular to the direction of the incident neutron beam in this position. Then the sample was rotated by an angle of 63° about the a axis and measured again. During this second measurement, $\boldsymbol{Q}$ therefore lay in the plane perpendicular to the a axis and formed an angle of 63° with the c axis. The angle of 63° was chosen because at higher angles the cadmium mask framing the sample container would have shielded the sample against incoming neutrons. The two measured INS spectra are presented in Fig. 2.

The intensity of one-phonon neutron scattering from hydrogen in a single crystal is proportional to the product $(\boldsymbol{Q}\boldsymbol{e}_H)^2$, where $\boldsymbol{e}_H$ is the polarization vector of the excited vibrational mode of hydrogen. In the case of the $ReH_{0.09}$ single crystal with the c axis parallel to $\boldsymbol{Q}$, the integrated intensity of both the fundamental optical peak at $\omega_2 = 130$ meV and of its low-energy shoulder are smaller by orders of magnitude than in the case of the powder sample [Fig. 2(a)]. Evidently, the corresponding optical H modes are predominantly polarized in the basal plane, perpendicular to the c axis. On the other hand, the integrated intensity of the fundamental peak at $\omega_1 = 100$ meV is drastically reduced compared to the powder case when the angle between $\boldsymbol{Q}$ and the c axis of the single crystal is 63° [Fig. 2(b)]. This indicates that the 100 meV optical modes are predominantly polarized along the c axis. The assignment of the fundamental peaks at 100 and 130 meV to optical H vibrations polarized along and perpendicular to the c axis, respectively, also agrees with the angular variation of the intensities of peaks in the higher optical bands of the $\mathrm{ReH}_{0.09}$ single crystal.

However, while the occurrence of a splitting of the fundamental H optical band in $\mathrm{ReH}_{0.09}$ is in accordance with the crystal symmetry of the Re-H solid solutions, the large magnitude of the effect is difficult to explain. The problem is that the axial ratio of the hcp rhenium lattice in these solutions[7,9] is close to the ideal value of $c/a = \sqrt{8/3} \approx 1.633$, so that the hydrogen atoms occupy octahedral interstices with nearly cubic local symmetry, which are formed by six rhenium atoms sitting at apices of nearly ideal octahedrons. In the case of cubic site symmetry, the peak of hydrogen local vibrations should be threefold degenerate. In a dynamical model assuming only harmonic longitudinal forces acting along the lines connecting one hydrogen atom with the six nearest rhenium atoms, the experimentally observed ratio $\omega_1/\omega_2 = 100/130$ for excitations along the c axis and perpendicular to it requires $c/a = (\omega_1/\omega_2)\sqrt{8/3} \approx 1.256$. In the Re-H solid solutions[7,9] however, the axial ratio varies only from $c/a = 1.615$ at $x = 0$ to $c/a \approx 1.591$ at $x = 0.22$.

A splitting of the fundamental optical band into two peaks, one polarized along the c axis and the other in the basal plane, has been observed previously in the INS spectra of hydrogen and deuterium solutions in rare-earth metals, Y-H and Y-D,[11–14] Sc-H,[14,15] and Lu-D,[14] in which H and D atoms occupy tetrahedral interstices of the hcp metal lattice. The c/a ratios of all these solutions and the values of ω_1 and ω_2 of the Y-H and Sc-H solutions are close to those for $\mathrm{ReH}_{0.09}$ with octahedral hydrogen. At the same time, the spectra of the solutions with tetrahedral hydrogen are different in some other aspects: The optical hydrogen vibrations along the c axis are significantly anharmonic and at low temperatures the fundamental peak of these vibrations is broadened in Sc-H and is split by about 4 meV in Y-H. In the case of $\mathrm{ReH}_{0.09}$, the vibration along the c axis by itself shows largely harmonic behavior, and the corresponding peak shows no broadening, its width being determined entirely by the energy resolution of the spectrometer. The broadening and the small splitting of the first fundamental peak in the INS spectra of hydrogen solutions in the rare-earth metals was attributed to pairing of hydrogen atoms on the next-nearest tetrahedral sites bridged by a metal atom along the c axis.[13] So far, however, there is no theoretical explanation of the large splitting of the fundamental optical band of these solutions into two peaks of vibrations along the c axis and in the basal plane.

C. Neutron diffraction from $\mathrm{ReH}_{0.09}$ powder

To examine $\mathrm{ReH}_{0.09}$ for a possible hydrogen superstructure or large random displacements of the hydrogen atoms from the centers of the octahedral sites—two potential reasons for the observed splitting of the fundamental optical band—the powder sample was studied by neutron diffraction at 90 K. The obtained neutron spectrum was analyzed using the Rietveld profile refinement technique implemented in the DBWS-9411 computer program.[16]

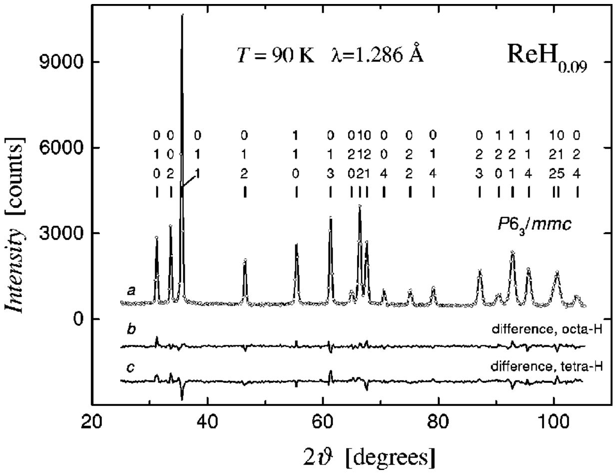

FIG. 3. Neutron diffraction pattern of $\mathrm{ReH}_{0.09}$ powder (circles) measured at 90 K and results of its Rietveld analysis (solid lines). Curve a is the profile calculated for hydrogen on octahedral interstices. Curve b is the difference between the experimental (circles) and calculated (curve a) spectra. Curve c is the difference between the experimental spectrum and that calculated for $x = 0.09$ hydrogen atoms randomly occupying tetrahedral interstices in the hcp metal lattice of $\mathrm{ReH}_{0.09}$, the other fitting parameters being the same as for the octahedral model.

The spectrum is shown in Fig. 3 and can be indexed with a hexagonal unit cell with the parameters $a = 2.7688(5)$ Å, $c = 4.4559(8)$ Å, and $c/a = 1.6093(4)$. It contains no new lines in addition to the lines of the hcp structure. The crystal structure of $\mathrm{ReH}_{0.09}$ therefore belongs to the same space group, $P6_3/mmc$, as the hcp structure of its metal lattice, and shows no long-range order in the hydrogen sublattice.

In the hcp structure there are two types of highly symmetrical interstitial sites conforming to the $P6_3/mmc$ space group, the octahedral and tetrahedral positions. Despite the low hydrogen concentration in the sample and the large coherent neutron scattering cross section of rhenium (10.6 barn) compared to that of hydrogen (1.76 barn), the analysis of the neutron diffraction spectrum shows with certainty that hydrogen in $\mathrm{ReH}_{0.09}$ occupies octahedral sites. In fact, with the expected profile factor $R_{\mathrm{ex}} = 3.57\%$, a model with no hydrogen gives a profile factor $R_p = 4.04\%$, while a model with hydrogen randomly distributed over octahedral sites gives $R_p = 3.72\%$ and yields an optimum H/Re atomic ratio of $x_{\mathrm{fit}} = 0.088$, which is close to $x = 0.094$ determined by hot extraction. At the same time, a model with $x = 0.09$ hydrogen atoms randomly occupying tetrahedral sites gives $R_p = 4.95\%$, and the solution converges to $x_{\mathrm{fit}} = 0$ and $R_p = 4.04\%$ if the hydrogen content is allowed to vary as a fitting parameter.

The neutron diffraction data also appeared sufficient for the conclusion that along the c axis the hydrogen atoms are not subject to significant displacements, Δz, from the centers

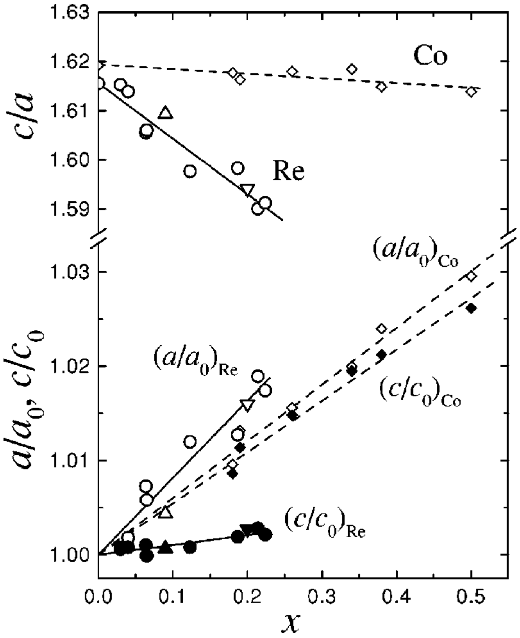

FIG. 4. The axial ratio, c/a, and relative values of the parameters, a/a_0 and c/c_0, of the hcp metal lattice of hydrogen solid solutions in rhenium at 90 K (circles and triangles) and of hydrogen and deuterium solid solutions in cobalt at 120 K (diamonds) as a function the H(D)/Me atomic ratio x. The circles show the x-ray data of Ref. 7. The down triangles, up triangles, and diamonds present the neutron diffraction data of Ref. 9, of the present paper, and of Ref. 2, respectively. a_0 and c_0 are the values of the lattice parameters at $x=0$. The solid and dashed lines show linear least-squares fits to the data for the Re-H and Co-H solutions, respectively.

of the octahedral sites. In this case, the integral factor R^I was most sensitive and it varied from 2.03% for $\Delta z=0$ to 2.80% for $\Delta z=0.24$ Å, and to 3.83% for $\Delta z=0.36$ Å. Thus, like $ReH_{0.2}$ studied earlier,[9] $ReH_{0.09}$ can be considered as a disordered solid solution of hydrogen randomly occupying positions at the centers of octahedral interstices in the hcp metal lattice.

Nevertheless, there seems to be at least one structural feature that distinguishes hydrogen solutions in rhenium from the solutions in other group VI–VIII transition metals. As seen from Fig. 4, the lattice expansion due to the hydrogen uptake is much more anisotropic for hcp rhenium than for hcp cobalt. Similar to rhenium, cobalt forms a continuous series of solid solutions with hydrogen on octahedral sites, but the Co-H solution shows no splitting of the optical hydrogen band.[4] The significant decrease in the c/a ratio of Re-H solutions with increasing hydrogen concentration agrees qualitatively with the higher energy of optical H vibrations in the basal plane than along the c axis, as found in the INS experiment. In fact, the higher vibrational energy indicates stronger H-Re interactions in the basal plane, and, being repulsive, those should lead to a larger relative increase in the a parameter on hydrogenation.

Interestingly, the c/a ratio of pure Re metal at room temperature is virtually independent of pressure up to 216 GPa, though the unit cell volume of the metal decreases by as much as 26.6%.[17] This suggests nearly isotropic Re-Re interactions in Re without hydrogen. In view of the nearly cubic local symmetry of octahedral interstices randomly occupied by hydrogen, neither the anisotropic lattice expansion of rhenium on hydrogenation, nor the large splitting of the optical H modes in the Re-H solution can therefore be attributed to an anisotropy in the elastic properties of Re metal itself. These effects must rather result from specific H-Re interactions.

IV. SUMMARY

The experiments show that at a temperature of 90 K, $ReH_{0.09}$ is a disordered solid solution of hydrogen randomly occupying positions at the centers of octahedral interstices in the hcp rhenium lattice. Despite the nearly cubic local symmetry of the hydrogen positions, the fundamental band of optical hydrogen vibrations at 5 K and 90 K is split into two peaks centered at 100 and 130 meV. The narrow peak at 100 meV arises from nearly nondispersive modes of hydrogen vibrations along the c axis of the crystal lattice. The peak at 130 meV has a strong low-energy shoulder, both attributable to hydrogen vibrations in the basal plane. Hydrogen vibrations along the c axis and in the basal plane show an approximately harmonic behavior in the fundamental and in the second optical band. Hydrogen vibrations in other directions are strongly anharmonic at energies above the fundamental band. The observed large splitting of the H vibrational modes with different polarizations finds no satisfactory explanation yet.

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