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Molecular dynamics of a dilute solution of hydrogen in palladium

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Molecular-dynamics results on a dilute solution of H in Pd are presented and compared with available incoherent inelastic neutron-scattering results. The embedded-atom model adopted here does a good job of describing the H-Pd atomic forces probed by incoherent inelastic neutron scattering. The time correlation functions associated with the computed spectra are strongly damped and indicative of the anharmonicity that has been suggested as the principal contribution to the anomalous isotope dependence of the superconducting transition temperature in PdH. These results highlight the fact that the H-atom vibrations in Pd-H solutions are low-frequency, large-amplitude vibrations relative to vibrations of H atoms in usual covalent interactions. The rms displacement of the H atom from its mean position in the center of the Pd octahedron compares favorably with the available neutron-diffraction results.

I. INTRODUCTION

This paper presents molecular-dynamic simulation results for a dilute solution of hydrogen in palladium and compares the predicted motion of the hydrogen in the octahedral interstitial site with the available incoherent inelastic neutron-scattering results.[1-4] These calculations benefit from current advances in the description of interatomic forces in metallic solutions.[5-7] Because these calculations focus on dynamical properties for which measured and computed quantities can be simply and directly compared, they provide a new test of the efficacy of the model force law used. Such a test is clearly a prudent step preparatory to atomically detailed theoretical studies of more global thermal properties of hydrogen-metal solutions such as phase transitions and more macroscopic transport processes. Furthermore, these results should be of guidance in describing interatomic forces in more complex metallic systems not satisfactorily treated by the current models.

Incorporation of hydrogen into metals elicits several phenomenon of intrinsic interest, for example, embrittlement of the metal. The hydrogen-palladium system has probably been studied more extensively than any other metal hydride. It displays unusual isotope effects on temperatures of transition to superconductive behavior.[8] Phonon-dispersion relations have been measured by inelastic neutron scattering for concentrated PdH_x sytems,[9] and these phonon spectra have been modeled by lattice-dynamical calculations.[10] Molecular-dynamics calculations have been carried out previously[11] on an empirical pairwise force model of PdH_x in supercritical thermodynamic states.[12] Under those conditions much of the interest in PdH_x is associated with the transport phenomena typified by fast ion conductors.

The next section records procedural details of the molecular-dynamics calculations. Secion III then presents and discusses the results. The final section notes the conclusions drawn from these calculations.

II. MOLECULAR-DYNAMICS METHODS

The calculations were carried out for a system of 256 Pd atoms and one H atom. The Pd atoms were situated initially in a fcc lattice with a lattice constant of 3.89 Å and the H atom was placed in an octahedral interstitial site. The embedded-atom model description of interatomic forces presented in Ref. 5 was used without modification except that the model atomic electron densities were smoothly truncated on a sphere of radius 7.780 Å. This latter distance corresponds to one-half the edge length of the cubical simulation cell within which the interaction potential energies and the interatomic forces were computed with the usual periodic boundary conditions. The model atomic electron densities were modified on the segment (6.675,7.780 Å) by substitution with a cubic spline which vanished with zero derivative at the outer boundary. The equations of motion were integrated by the explicit central difference method,[13] or summed Verlet method.[14] The estimated standard error was obtained by assuming that distinct 20 ps blocks of trajectory were independent samples of the property in question.

III. RESULTS

The mean kinetic energy of the system over our observation yields a temperature estimate of (297±6) K. The predicted pressure of $pV/Nk_BT=(0.01\pm0.02)$ was realistically low. It is known from experiment that H vibrational motions in Pd occur at frequencies which are low compared to those of H vibrations in usual covalent interactions.[1-4] Therefore, at this temperature the H motions may be expected to be largely classical in character, although quantum-mechanical characteristics are easily observed. This expectations can be tested simply and quantitatively in the context of the present calculations. In particular, the initial quantum-mechanical correction to the classical-mechanical Helmholtz free energy of the system is[15]

$$\beta A=\beta A_{\mathrm{cm}}+\tfrac{1}{8}\sum_{j=1}^{N}(\beta\hbar\Omega_j)^2+\mathrm{o}(\hbar^2)\ . \tag{1}$$

Here, A is the Helmholtz free energy and A_{cm} is that free energy obtained from the classical phase-space integral; $\beta=(k_BT)^{-1}$ is the inverse temperature in energy units. The frequency Ω_j is

$$\Omega_j^2=\frac{\beta\langle F_j^2\rangle}{3m_j}\ , \tag{2}$$

where $\langle F_j^2\rangle$ is the mean-square force on particle j and m_j is the mass of that particle. The frequency Ω_j can also be obtained from observation of the classical motion of the jth particle through use of the sum rule

$$\Omega_j^2=\frac{\int_{-\infty}^{\infty}d\omega\,\omega^2|v_\omega|^2}{\int_{-\infty}^{\infty}d\omega|v_\omega|^2}\ . \tag{3}$$

Here we have used the notation

$$|v_\omega|^2=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,\cos\omega t\langle v(0)v(t)\rangle/\langle v\rangle\ , \tag{4}$$

where $\langle v(0)v(t)\rangle$ is the autocorrelation of the velocity of the particle. With this definition the denominator appearing in Eq. (3) is equal to 1. The present calculations produce the estimate $\Omega_{\mathrm{H}}=(97\pm13)$ meV for the H-atom solute. This is only a factor of 5 larger, approximately, than the correspondoing frequency for the Pd atoms (averaged over all the Pd atoms), $\Omega_{\mathrm{Pd}}=(21.2\pm0.02)$ meV. The ratio of the frequencies is therefore considerably smaller than the square root of the ratio of the masses, $\sqrt{106}$. This implies that the forces on the H solute are typically considerably less then the forces which localized the Pd atoms in the fcc solid. This situation is reflected in the fact that the rms displacement of the H atom from its mean position in the center of the octahedral hole is quite substantial: $[\frac{1}{3}(\langle r_{\mathrm{H}}^2\rangle-\langle r_{\mathrm{H}}\rangle^2)]^{1/2}=(0.138\pm0.005)$ Å, where r_{H} is the position of the H atom. This is consistent with the value of (0.25 ± 0.10) Å obtained by neutron diffraction on dilute PdH_x samples in the neighborhood of 600 K.[16] The larger value of the measured quantity is understood as a result of the higher temperature state studied by the available experiments. The ratio of these two quantities is consistent with a $\sqrt{T}$ temperature dependence but the size of the estimated errors on the experimental values does not permit a stronger conclusion.

A. Neutron vibrational spectroscopy

The vibrational spectrum of the H-atom motion dissolved at low concentrations in Pd has been measured by incoherent inelastic neutron scattering.[1,2] These experiments provide directly the Fourier transform of the autocorrelation function[17]

$$F_s(\mathbf{k},t)=\langle\exp[i\mathbf{k}\cdot\mathbf{r}_{\mathrm{H}}(t)]\exp[-i\mathbf{k}\cdot\mathbf{r}_{\mathrm{H}}(0)]\rangle\ . \tag{5}$$

For $|\mathbf{k}|$ sufficiently small, we can write

$$F_s(\mathbf{k},t)=1+k_\alpha k_\gamma\langle\delta r_{\alpha\mathrm{H}}(t)\delta r_{\gamma\mathrm{H}}(0)\rangle+\mathrm{o}(k^2)\ , \tag{6}$$

where $\delta r_{\alpha\mathrm{H}}(t)=r_{\alpha\mathrm{H}}(t)-\langle r_{\alpha\mathrm{H}}\rangle$ and $r_{\alpha\mathrm{H}}(t)$ is the αth Cartesian component of the instantaneous position of the H atom. The octahedral site of the H atom has cubic symmetry; the mean position is a center of inversion symmetry and each Cartesian axis is symmetric with the others. Therefore

$$\langle\delta r_{\alpha\mathrm{H}}(t)\delta r_{\gamma\mathrm{H}}(0)\rangle=\begin{cases}\langle\delta x_{\mathrm{H}}(t)\delta x_{\mathrm{H}}(0)\rangle & \text{if } \alpha=\gamma\ ,\\ 0 \text{ otherwise}\ , & \end{cases} \tag{7}$$

and

$$F_s(\mathbf{k},t)=1+k^2\langle\delta x_{\mathrm{H}}(t)\delta x_{\mathrm{H}}(0)\rangle+\mathrm{o}(k^2)\ . \tag{8}$$

Under the conditions of the available experiment[1] $|\mathbf{k}|=4.9$ Å. Therefore, $k^2\langle\delta x_{\mathrm{H}}^2\rangle=0.8$, and the approximation of Eq. (8) is likely to be reasonable but deserves checking. Figure 1 shows the time correlation functions identified in Eqs. (5) and (8). On the 100 fs time scale associated with the decay, these quantities are strongly similar. The results for $F_s(\mathbf{k},t)$ for nonzero values of $|\mathbf{k}|$ were obtained by orienting $\mathbf{k}$ along a Cartesian axis but averaging over all the vectors in the star of $\mathbf{k}$. Since the results obtained are not qualitatively changed by changes of $|\mathbf{k}|$ in this regime, it is reasonable to assume that orientational averaging also would not change the results qualitatively. We note that on this time scale, these atomic motions are strongly damped.

The spectra of these correlation functions are shown in Fig. 2 over the same range and with approximately the same resolution with which the experimental spectrum are available. The experimental spectrum is shown in Fig. 3. The center of each of these spectra is very close to the center of the measured spectra. The experimental spectrum also shows a shoulder (or perhaps a broad background) extending to higher energy, as do the computed results. However, this is considerably more prominent in

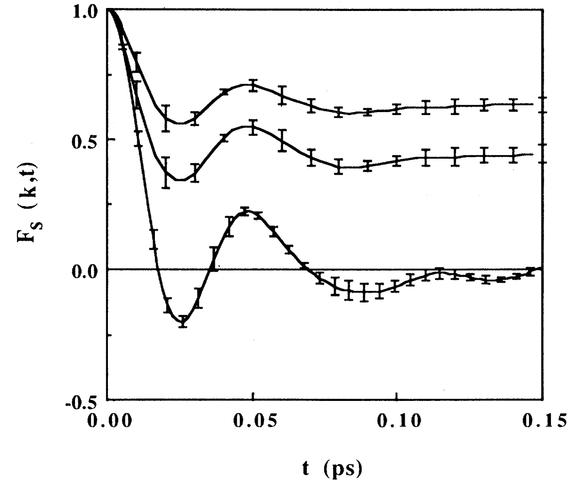

FIG. 1. Time correlation functions associated with the H solute vibrational motion. Upper curve, $F_s(\mathbf{k},t)$ with $|\mathbf{k}|=4.9$ Å; middle curve, $F_s(\mathbf{k},t)$ with $|\mathbf{k}|=6.5$ Å; lower curve, $\langle\delta x_{\mathrm{H}}(0)\delta x_{\mathrm{H}}(t)\rangle/\langle\delta x_{\mathrm{H}}^2\rangle$.

the calculation than in the experiment. These features have been described as due to multiphonon processes.[1] The present calculations allow us to refine this characterization. Since this background is not strongly dependent on $|\mathbf{k}|$ in this range, we conclude that this background is not due principally to excitation by the neutron of many phonons at once.[18] However, these strongly damped correlation functions reflect anharmonic dynamics in which numerous phonons interact strongly during the relaxation. The experimental results also show appreciable intensity between 140 and 170 meV, which is associated with quantized overtone transitions for the H vibration. This is not present in the classical mechanical calculation. However, the intensity in the region between 90 and roughly 120 meV, which does appear to diminish for the $|\mathbf{k}| \to 0$ spectrum, is likely a reflection of these overtone processes, although described classially.

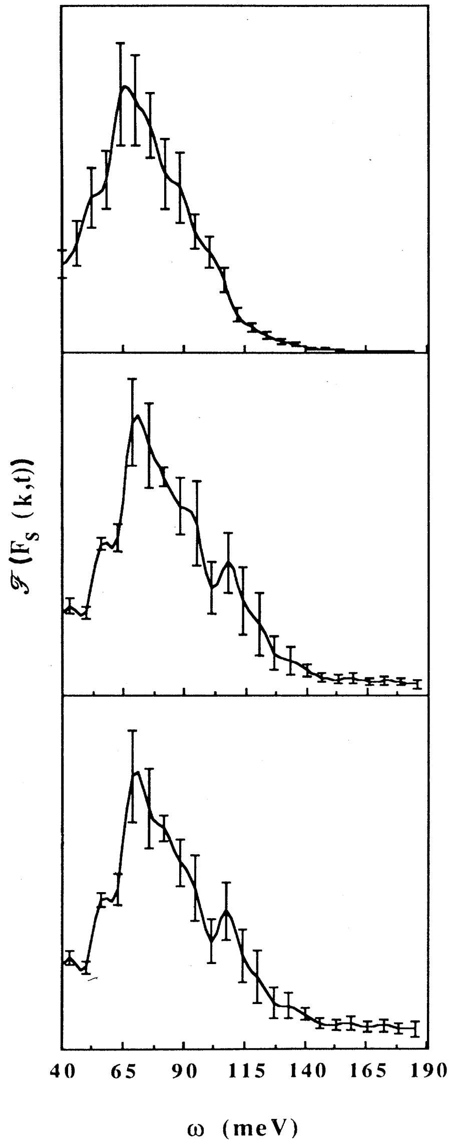

FIG. 2. Fourier transforms $\mathcal{F}$ of the correlation functions shown in Fig. 1. From top to bottom: $|\mathbf{k}| = 0(|\delta x_\omega|^2)$; $|\mathbf{k}| = 4.9$ Å; $|\mathbf{k}| = 6.5$ Å. These results are displayed over the same range and with approximately the same resolution as the measured spectra of Ref. 1.

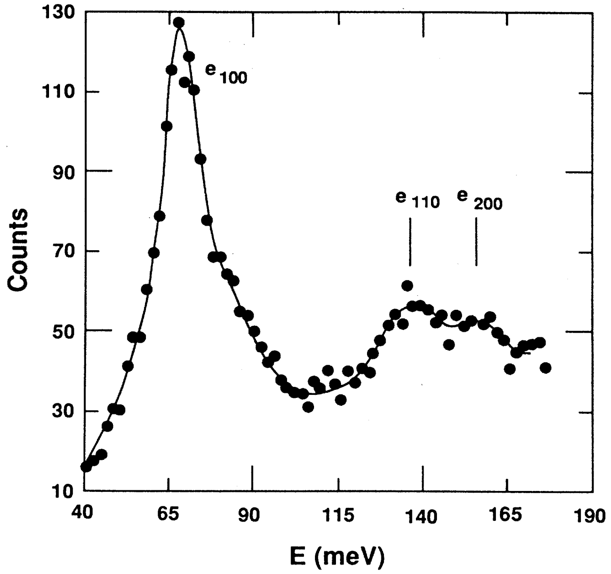

FIG.3. Vibrational spectrum of $PdH_{0.04}$ by measured incoherent inelastic neutron scattering, redrawn from D. Richter [Los Alamos National Laboratory Report No. LA-10227, 1984, p. 559 (unpublished)]. See also Ref. 1.

These computed spectra are sufficiently broad that identification of a fundamental frequency might be ambiguous without some detailed consideration of the line shape. This is exemplified by the power spectrum $|v_\omega^2|$ of the H-atom velocity of Fig. 4. This line shape differs for the Fourier transform of $\langle \delta x_H(t) \delta x_H(0) \rangle$ by only a factor of ω^2. But the quantitative similarity between the molecular-dynamics results and the experiment would be

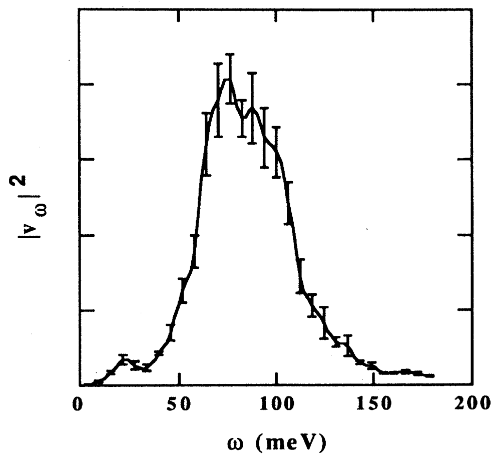

FIG. 4. Power spectrum of the velocity of the H solute.

significantly clouded if the function of Fig. 4 only were to be compared with the measured spectrum. Preliminary calculations which varied the mass of the impurity verified that these computed spectra do, indeed, shift with the square root of the solute mass, as expected.

The power spectrum of Fig. 4 also can provide the frequency Ω_H noted above. The determination of this frequency allows us to test the description of the thermodynamic properties afforded by Eq. (1). In particular, we define a Sievert's law constant, $k_s(\mathrm{H})$, for hydrogen dissolution by

$$k_S(\mathrm{H})=\lim_{x_\mathrm{H}\to 0}(x_\mathrm{H}/\sqrt{p_{\mathrm{H}_2}}) \ , \qquad (9)$$

where x_H is the mole fraction of hydrogen (H) in the metal and p_{H_2} is the pressure of hydrogen gas (H_2) in the vapor phase. We then inquire about the ratio $[k_S(\mathrm{H})/k_s(\mathrm{D})]$. The differences of the gas phases, H_2 versus D_2, makes a very large contribution to this ratio. This contribution can be obtained from textbook material.[19] The nonclassical character of the atomic motion in the metal which is identified by Eq. (1) contributes a factor of

$$\exp\left[\frac{1}{8}\left[\frac{m_\mathrm{H}-m_\mathrm{D}}{m_\mathrm{D}}\right](\beta\hbar\Omega_\mathrm{H})^2\right]\approx 0.4 \ .$$

This gives rise to an estimate of $[k_S(\mathrm{H})/k_S(\mathrm{D})]\approx 1.1 \pm 0.3$. This is approximately 40% smaller than the experimental value.[20]

In view of the satisfactory agreement between the computed and measured vibrational spectrum for the H impurity, it seems likely that this discrepancy between the computed and measured differential solubility of H versus D indicates that the simplest description of the quantum mechanics, Eq. (1), is not satisfactorily accurate for the sytem under the present conditions. Ideas for numerically exact calculation of such effects have been the focus of recent research. Suitable basic approaches for these tasks have been clearly articulated and successful applications have been presently already.[21–23] However, detailed implementations differ with the details of the different problems which have been considered. We expect to return to this issue with subsequent work.

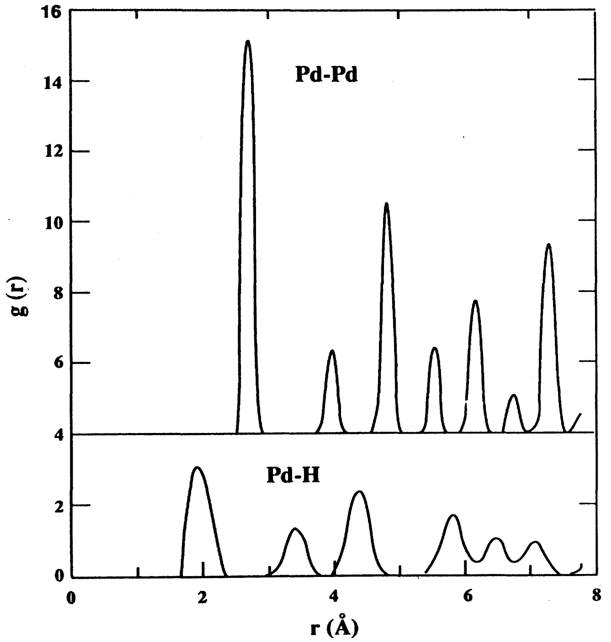

FIG. 5. Radial distribution functions for Pd-Pd and Pd-H pairs.

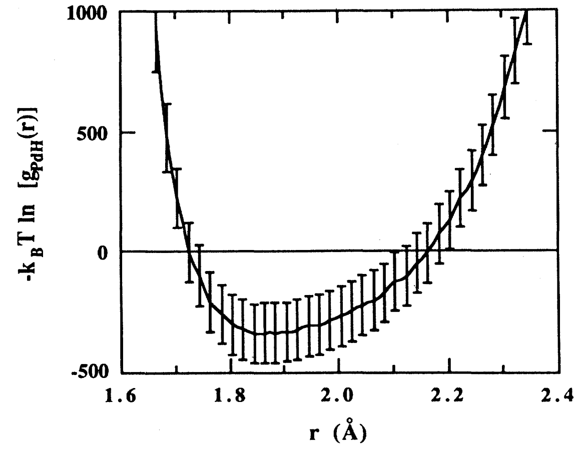

FIG. 6. Potential of the average forces directed between Pd-H pairs. The energy unit is the kelvin, i.e., $k_B=1$.

B. Equilibrium structure

The radial distribution functions obtained from these calculations appear in Fig. 5. The expected and observed features of the Pd-H radial distribution are considerably broader than those of the Pd-Pd distribution. This is associated with the above observation that the H atom vibrational motion is a low-frequency, large-amplitude motion compared to H vibration under typically covalent interactions. The rms displacement of the H atom which characterizes the Debye-Waller factor was given above and compared with experimental values. An alternative way of displaying the relatively large amplitude of the H atom motions is given in Fig. 6. There the Pd-H potential of mean force is plotted. This free energy surface is remarkably slowly varying over a spatial region within 0.1 Å of the expected crystallographic displacement of 1.945 Å

IV. CONCLUSIONS

The embedded-atom model adopted here does a good job of describing the H-Pd atomic forces probed by incoherent inelastic neutron scattering. The results highlight the fact that the H atom vibrations in PdH solutions are low-frequency large-amplitude vibrations relative to vibrations of H atoms in usual covalent interactions. The rms displacement of the H atom from its means position in the center of the Pd octahedron compares favorably with the available neutron-diffraction results. The solubility differences between H and D are not accurately described by the present calculation. This likely due to the perturbative treatment of the quantum-mechanical corrections to the thermodynamic properties which has been tested here. In subsequent work, we expect to study the solubility of these isotopes with numerical path-integral methods for description of the quantum-mechanical nature of the H motion under these conditions.

The anharmonic character of the dynamics studied here deserves emphasis. It has been argued that this anharmonicity is the principal contribution to the anomalous isotope dependence of the superconducting transition temperature in PdH.[1] Furthermore, atomic level theoretical investigations of the phase transitions and transport processes of hydrogen metal systems require an accurate description on the interatomic forces not limited to harmonic interactions. Most of the previous dynamical calculations on PdH_x have focused on the development of lattice-dynamical models from the measured phonon-dispersion relations.[10] Theoretical calculations similar to the present work which test the accuracy of the available electron gas models for forces among hydrogen constituents at higher concentrations would be a natural next step. Subsequent attention given to systems such as TiH_x in which more complex metal behavior accompanies and intrudes upon dissolution of the hydrogen would also be helpful.

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