DOE/ET-53088-376 IFSR #376

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June 1989

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(Received)

Screening action of the hybridized 4d-1s electrons in PdD_x is analyzed in the Fermi-Thomas approximation; charge-form factors for Pd and D are derived. The resulting D-D interaction is a sensitive function of both density x of the deuterons and energy levels E_{1s} of D-induced s-electron states; it exhibits an attractive part arising from interference between the 1s-screening electrons and strongly coupled ($r_s \simeq 2$) valence electrons. Nuclear reaction rates of hydrogen isotopes in Pd are calculated at various combinations of x and E_{1s} by including D-D many-body effects through the ion-sphere potential; effects of fluctuations in x and/or E_{1s} are discussed.

PACS numbers: 24.90.+d, 71.45.Jp

Possibility of nuclear fusion between isotopic hydrogen nuclei in a laboratory condensed matter through electrolysis[1,2] or through the absorption/desorption processes[3] has prompted us to investigate how two positively charged nuclei such as deuterons come to fuse by overcoming the Coulombic repulsive forces in such an environment. In an earlier report,[4] we have shown that in a heavily deuterated palladium metal (PdD_x) a pair of deuterons exhibit attractive interaction at short distances (0.1Å - 0.7Å) due to strong Coulomb correlations in the ion-sphere model and due to screening by the hybridized 4d-1s electrons; the rates of enhanced thermonuclear reactions at room temperatures have thus been elucidated.

In this Letter, we carry out Fermi-Thomas analyses of the screening action of the 4d-1s electrons coupled with the f-sum rules, calculate the effective masses of such screening electrons, and thereby derive the charge-form factors of ionic nuclei for Pd and D. The resulting D-D interaction, containing an attractive part due to strongly coupled valence electrons,[5] depends sensitively on the deuteron density and the energy levels of those s-electron states which are induced by deuterons around the octahedral sites of the fcc Pd crystals. We take account of D-D many-body effects via the ion-sphere potential[5,6] of strongly coupled plasmas, to predict the rates of nuclear reactions between hydrogen isotopes in a metal such as PdD_x.

We begin with an f-sum rule expression[7] for the frequency-dependent dielectric function,

$$\varepsilon(\omega) = 1 - \Sigma_j \frac{4\pi n_j e^2}{m} \frac{1}{\omega^2 - \omega_j^2} \qquad (1)$$

where m is the bare mass of an electron, n_j and $E_j = \hbar\omega_j$ refer to the number density and excitation energy of the electrons in the j-level.

Since $\omega \ll \omega_j$ at a room temperature T, the dielectric constant of our concern is

$$\varepsilon(0) = 1 + 4\pi \sum_j n_j/E_j^2 , \qquad (2)$$

where and in what follows we use the atomic units ($m = e^2 = \hbar = 1$) unless specified otherwise. It has been shown[3] by this formula that the contribution of $(4s)^2(4p)^6$ electrons in the Kr-core of Pd produces a core dielectric constant $\varepsilon_c = 1.25$ for the number density of palladium, $n_{Pd} = 6.25 \times 10^{22}$ cm^{-3}, corresponding to a lattice constant, 4Å.

Photoemission studies[8,9] of the Pd/H system have shown a band of hydrogen-induced energy states centered at 1 eV below the bottom of Pd-derived 4d bands of width 4.4 eV. We assume the same state-density structures applicable to a PdD_x system with $x \simeq 1$. It has been pointed out[4] that a band width $\Delta E_{4d} \simeq 4$ eV would lead to a band mass $m_b \simeq 7$ for the ten (per atom) Pd-derived d-electrons. Analogous calculation with $\Delta E_{1s} \simeq 1 - 2$ eV would give an estimate $m_b \simeq 3 - 6$ for the D-induced s-electrons.

Let us first analyze the screening effect of ten 4d-electrons of Pd by separating them into ν_{4d} *screening* electrons and Z (= 10 - ν_{4d}) *valence* electrons. The latter electrons are those occupying the states near the Fermi surface; observations[8-10] of the density of states and the specific heats have indicated their effective masses in the vicinity of the bare mass. We assume Z = 2 - 3 for Pd.

In a *partial system* consisting of Pd ions (i.e., Pd nuclei plus the Kr-core electrons) and their screening and valence electrons, the static dielectric constant for the 4d-screening electrons is then calculated from Eq. (2) as

$$\varepsilon_{4d} = 1 + 86\nu_{4d}/[E_{4d}(eV)]^2 . \quad (3)$$

Assuming $\nu_{4d} = 8$ and $E_{4d} = 4$ eV, we find $\varepsilon_{4d} = 44$.

Since $\nu_{4d} \gg 1$, we adopt the Fermi-Thomas continuum model[11] for an approximate representation of the screening electrons around a Pd ion. The screening constant for the electrons with density $n_{4d} = \nu_{4d} n_{Pd}$ and effective mass m_{4d} is then given by

$$k_{4d} = 1.7 \times 10^8 \ \nu_{4d}^{1/6} \ m_{4d}^{1/2} \qquad (cm^{-1}) . \quad (4)$$

For internal consistency of such a screening picture, we require that the k_{4d} be greater than the inverse radius of a (hypothetical) 5s electron around a Pd ion, which in turn is equal to or greater than Z. We thus find that the lower bound of m_{4d} in this model is around 8 at Z = 1 and increases with Z. We take this finding together with the band-mass estimates cited above as an evidence suggesting that the 4d-screening electrons are highly localized objects with effective masses, $m_{4d} > 7$.

At a distance sufficiently greater than 1/Z, the 4d-screening electrons should produce a (homogeneous) screening effect represented by ε_{4d}. Retaining this requirement, we derive the charge-form factor of a Pd ion in the wave number (k) space arising from the spatial distribution of 4d-screening electrons as

$$f_{Pd}(k) = [Z_0 + \nu_0 k^2 / (k^2 + k_{4d}^2)] / Z_{Pd} \quad (5)$$

where $Z_0 = Z + \nu_{4d}/\varepsilon_{4d}$ is the effective valence of Pd, and $Z_{Pd} = Z_0 + \nu_0 = 10$.

We next consider the screening effect of a 1s-like electron around a deuteron, by separating it into ν_{1s} *screening* electrons and $1 - \nu_{1s}$ *valence* electrons. Again in a partial system of deuterons and their screening and valence electrons, the static dielectric constant via (2) is $\varepsilon_{1s} = 1 + 86\, x\nu_{1s}/[E_{1s}(\mathrm{eV})]^2$. The value of ν_{1s} can in fact be determined from the aforementioned requirement related to the homogeneous screening with ε_{1s}, that is, ε_{1s}^{-1} must be equal to that part of the deuteron charge, $1 - \nu_{1s}$, which remains unscreened. At $x = 0.75$ and $E_{1s} = 5.5$ eV , we thus find $\nu_{1s} = 0.53$.

Since the D-induced 1s-screening electrons with an effective mass m_{1s} are hybridized with the Pd-derived 4d-screening electrons, their specific volume is $(n_{4d} + x\nu_{1s}n_{Pd})^{-1} \simeq n_{4d}^{-1}$. Hence, the Fermi-Thomas screening constant for the 1s-screening electrons is

$$k_{1s} = 1.7\times10^{8}\ \nu_{4d}^{1/6}\ m_{1s}^{1/2} \qquad (\mathrm{cm}^{-1})\ . \qquad (6)$$

The screening constant of ν_{1s} 1s-Bohr electrons, on the other hand, is given by $k_s = m_{1s}\nu_{1s}$. Equating this with (6), we find $m_{1s} = 5.6$ when $\nu_{4d} = 8$ and $\nu_{1s} = 0.53$. This effective-mass value falls in the range of our band-mass estimates mentioned above.

Physical origin of such an increase in the effective masses of the D-induced 1s-screening electrons may be traced to a many-body effect arising from hybridization with the Pd-derived 4d-screening electrons, which acts to restrict their specific volume to n_{4d}^{-1}. The charge-form factor of a deuteron with the 1s-screening electrons thus takes the form,

$$f_D(k) = 1 - \nu_{1s} + \nu_{1s}k^2 / (k^2 + k_{1s}^2)\ . \qquad (7)$$

The origin of the D-induced s-states can likewise be understood in terms of the Wigner-Seitz model[5,11] of localized electrons in the charge density n_{4d}. In such a model the binding energy of an electron with a mass m_{1s} is given by the electrostatic self-energy minus the energies of the zero-point oscillations, i.e.,

$$E_{WS} = 9.21\,\alpha\,\nu_{4d}^{1/3} - 8.04\,(\nu_{4d}/m_{1s})^{1/2} \quad \text{(eV)} . \tag{8}$$

In a spherical model, $\alpha = 0.9$, a theoretical upper bound; bcc/fcc/hcp Coulombic Madelung energies suggest $\alpha = 0.896$, which we adopt here. For $\nu_{4d} = 8$ and $m_{1s} = 4$, we obtain $E_{WS} = 5.1$ eV; E_{WS} increases in Eq. (8) as m_{1s} does. These features agree with the predictions from Eq. (6) (see Table I below).

The density of valence electrons with mass m_V in PdD_x is now given by

$$n_e = [Z_0 + x(1 - \nu_{1s})]\, n_{Pd} = Z_e\, n_{Pd} \tag{9}$$

with the r_S parameter calculated as

$$r_S = (3/4\pi n_e)^{1/3}\, m_V = 2.95\, Z_e^{-1/3}\, m_V . \tag{10}$$

For $Z_e \simeq 3$ and $m_V \simeq m$, $r_s \simeq 2.0$. Since $r_s > 1$, additional screening effects of those valence electrons, represented by the wave number-dependent dielectric function[5] $\varepsilon_v(k)$, will create attractive interactions between deuterons at short distances when the local-field effects produced by strong electron-electron correlations are appropriately taken into account.[5,12]

Finally, in terms of the palladium and deuteron charge-form factors

and the dielectric screening function of the valence electrons, the potentials of binary interaction between ions of α and β species (α, β = Pd, D) are expressed in the Fourier components as

$$\Phi_{\alpha\beta}(k) = [4\pi Z_\alpha Z_\beta / k^2 \varepsilon_c \varepsilon_v(k)]\, f_\alpha(k)\, f_\beta(k) \tag{11}$$

with $Z_D = 1$. In the short-range limit (i.e., $k \to \infty$), $f_\alpha(k)$ and $\varepsilon_v(k)$ approach unity, so that $\Phi_{\alpha\beta}(k)$ reduce to the bare Coulombic interactions (in a dielectric medium with ε_c). This limiting behavior is particularly essential to $\Phi_{DD}(k)$ for a correct treatment of nuclear reactions.

Let us therefore look into the detailed features of the D-D interaction $\Phi_{DD}(k)$ as presented in Eq. (11). For E_{1s} = 5.5 eV and x = 0.75, the bare (i.e., unscreened) part of D-D interaction is reduced by a factor of $(1 - \nu_{1s})^2 = 0.22$; the remaining part is confined within a distance of $k_{1s}^{-1} = 0.18$ Å by the screening effect of localized 1s-electrons with $m_{1s} = 5.6$ when $Z_0 = 3$. Both of those fields are further subjected to the $\varepsilon_v(k)$ screening of the valence electrons.

We here point out that $\Phi_{DD}(k)$ is quite a sensitive function of both density x of the deuterons and energy levels E_{1s} of the D-induced s-electron states, as the screening parameters in Table I illustrate. Figure 1 shows the D-D interaction potential $\Phi_{DD}(r)$, the inverse Fourier transform of $\Phi_{DD}(k)$, at various values of E_{1s}; this energy quantifies a trapping characteristic of individual octahedral sites. We observe an attractive part created at outside the 1s-screening electrons; this attractive interaction is a consequence of interference between the 1s-screening electrons and valence electrons in Eq. (11).

To estimate how those potentials in Fig. 1 affect the rates of nuclear reactions, we take account of D-D many-body effects in the ion-sphere

potential,[5,6] that is, the increment in the Coulombic chemical potential of a reacting pair before and after a nuclear reaction. In so doing, we regard the second (screened) part of Eq. (7) as representing a hard-core interaction with a diameter d determined by the point of contact at a relative kinetic energy, $(2\nu_{1s}^2/d)\exp(-k_{1s}d/2) = T/2$, and then evoke the equivalence[5,13] between a hard-sphere system and a dense Coulombic system [cf. Eq. (5) in Ref. 13], to derive an effective charge associated with the screened part.[14] We thus find at T = 300 K

$$\Delta Z_{1s} = 1 - \nu_{1s} + 0.075\,(\eta/x)^{1/6}(1 + 2\eta)/(1 - \eta)^2 \qquad (12)$$

where $\eta = 0.033x[d(\text{Å})]^3$ refers to the packing fraction of the equivalent hard-sphere system.[15]

The nuclear reaction rate λ_{DD} per a pair of deuterons is calculated, as we did in Ref. 4, for the effective pair potential

$$\Phi(r) = \Phi_{DD}(r) - 1.17\alpha(\Delta Z_{1s})^{5/3}/\varepsilon_c a \qquad (r < 0.7\,a) \qquad (13)$$

where $a = (3/4\pi n_e)^{1/3}$. Table II lists the predicted values of the nuclear reaction rates in the cases of Table I with $\varepsilon_c = 1.25$ for various pairs of hydrogen isotopes.

The values of λ_{DD} in Table II, representing an enhancement some 30 to 50 orders of magnitude over those in a D_2 molecule, may be regarded as reasonably close to those suggested in the experiments[2,3] if $x \simeq 1$ can be assumed. Thus we have been able to show in a theory without a free (adjustable) parameter that an enhancement of such a magnitude can take place

by attractive interactions between deuterons and by the ion-sphere potential created in a Pd metal.

We remark that the calculated rates of reactions are extremely sensitive to the evaluation of the potential (13). The largest reaction rates, obtained in (D) and (F), are due mainly to the contributions of the ion-sphere potential, and as such may contain a certain degree of uncertainty. In Table II, we nevertheless observe a steep increase in the reaction rates as functions of x, which we take as a real and significant physical effect. This observation would then lead us to predict an important role played by fluctuations of x and/or E_{1s} in determination of the reaction rates: if a state with $x > 1$ (i.e., more-than-one deuterons in an octahedral site) is realized by local fluctuations, net nuclear-reaction rates will be greatly enhanced. We speculate that such fluctuations may be realized more easily in non-equilibrium experimental situations.[2,3]

Since the binary potentials of ionic interaction in PdD_x are given by Eq. (11), we can proceed further with a microscopic investigation of effective D-D interactions by taking account of lattice fields produced by Pd ions, together with many-body correlations and quasi-bound states developed in strongly coupled deuterons. Theoretical analyses in these directions are in progress.

We appreciate helpful discussions with Prof. A. Arima and Prof. H. Kamimura of the University of Tokyo and with Prof. J. Keto of the University of Texas on this and related subjects. The work was supported in part through Grants-in-Aid for Scientific Research by Japanese Ministry of Education, and by U. S. Department of Energy.

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14. Since the hard-core effect stems from strong repulsive forces between the 1s-screening electrons, the resulting values of ΔZ_{1s} may exceed

unity for x = 1. Such an effective increase of the ion-sphere potential by electronic screening has been shown analytically in, S. Tanaka and S. Ichimaru, J. Phys. Soc. Jpn **53**, 2039 (1984).

15. When the computed value of η exceeds 0.74, the maximum packing fraction, we take $\eta = 0.74$.

FIGURE CAPTION

FIG. 1 D-D interaction potential for the cases in Table I : dashed curve, (B); solid curve, (D); and dotted curve, (F).

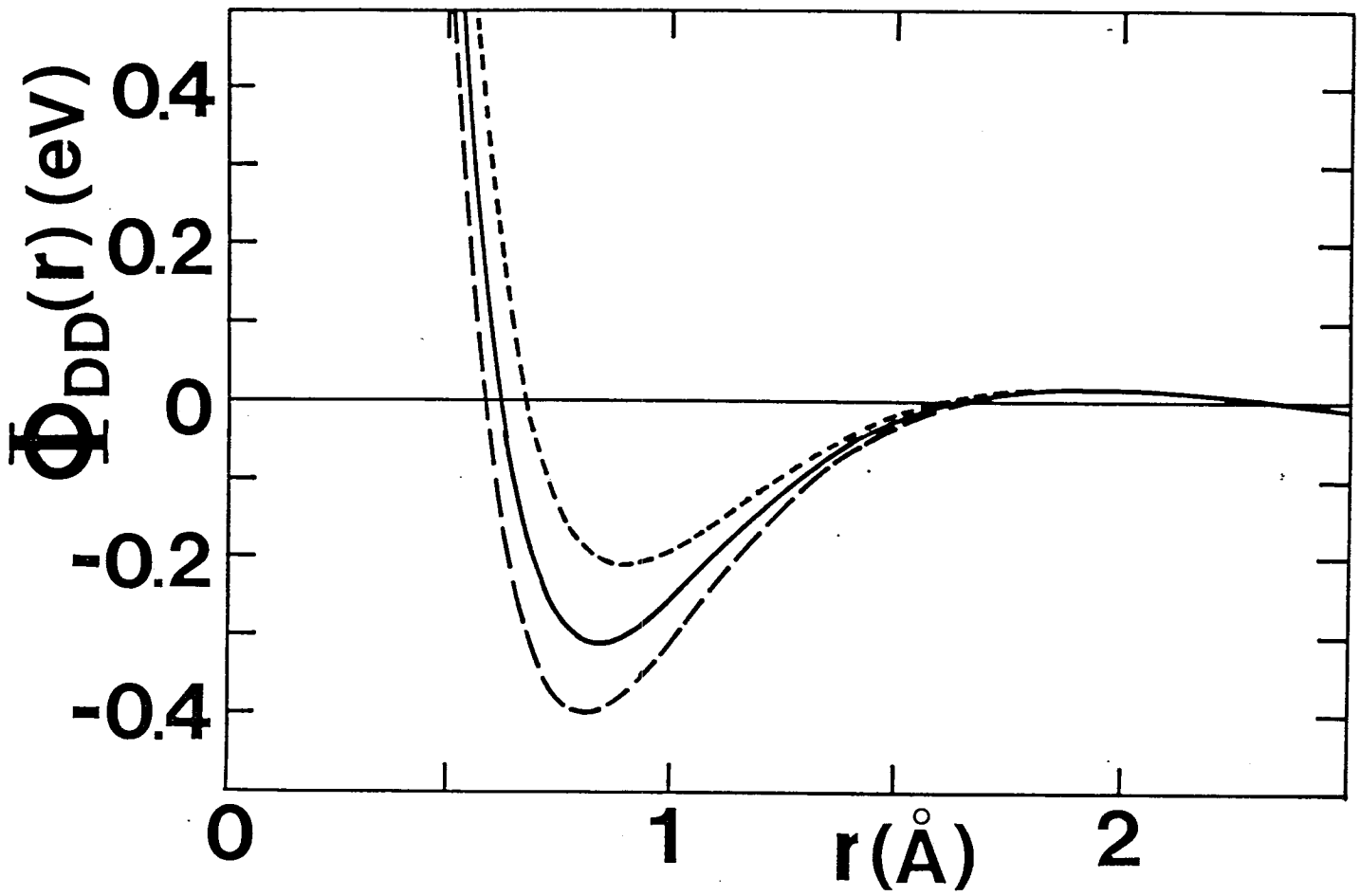

Fig. 1

TABLE I. 1s-screening parameters.

	E_{1s} (eV)	X	ν_{1s}	k_{1s}^{-1} (Å)	m_{1s}
(A)	4.5	0.75	0.69	0.23	3.4
(B)	4.5	1	0.77	0.26	2.7
(C)	5	0.75	0.61	0.21	4.2
(D)	5	1	0.71	0.24	3.1
(E)	5.5	0.75	0.53	0.18	5.6
(F)	5.5	1	0.65	0.22	3.6

TABLE II. Nuclear reaction rates in s^{-1}.

	λ_{DD}	λ_{PD}	λ_{DT}	λ_{PP}
(A)	1e-39	6e-36	4e-42	3e-48
(B)	1e-20	3e-20	2e-21	2e-34
(C)	7e-43	1e-38	9e-46	1e-50
(D)	4e-20	7e-20	6e-21	4e-34
(E)	1e-43	2e-39	1e-46	3e-51
(F)	4e-36	4e-33	2e-38	9e-46