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**Monte Carlo Simulation Study of Short-Range Correlations
Between Itinerant Hydrogen in Lattice Fields:
Application to "Cold Fusion"**

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We perform Monte Carlo simulation study for short-range correlations between itinerant hydrogen, interacting mutually via electron-screened repulsive forces, in periodic and aperiodic (due to defects) lattice fields of metal hydrides. We find that the screening potentials and the resultant fusion rates depend extremely sensitively on microscopic details in the lattice fields, corroborating qualitatively the varied results in recent "cold fusion" experiments.

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Observation of nuclear fusion reaction between itinerant hydrogen in metal hydrides (MH_x) claimed in recent experiments¹⁻³ has created a challenge to condensed matter physics, calling for a theoretical account of how two hydrogen nuclei can come to fuse by overcoming the Coulombic repulsive forces in such a metallic

environment. Other experiments^{4,5} performed under analogous settings, however, have not shown significant observation of nuclear reaction. One therefore speculates that the rate of nuclear reaction should depend extremely delicately on the states of reacting pairs at short distances.

The rate of fusion between hydrogen isotopes, a and b ($= p, d, t$), is proportional to $g_{ab}(0)$, the value of the joint probability density $g_{ab}(r)$ at $r = 0$ for the reacting pairs averaged over the motion of their center-of-mass and the remainder of the metal-hydride environment. The probability density can be factored as

$$g_{ab}(r) = g_{ab}^0(r) \exp[\beta H_{ab}(r)] \quad (1)$$

where $g_{ab}^0(r)$ represents the joint probability in the partial system consisting only of the reacting pair; β is the inverse temperature in energy units. Equation (1) defines the screening potential, $H_{ab}(r)$. Since the contribution of the direct interaction between a and b has been factored in (1), $H_{ab}(r)$ results from many-body effects in scattering with rest of the particles. It has been shown^{6,7} that the value of $H_{ab}(0)$ is equal to the increment in the interaction part of the chemical potential for the reacting pair before and after the nuclear fusion. It follows^{6,8,9} from Eq. (1) that the rate of fusion is enhanced by a factor, $\exp[\beta H_{ab}(0)]$, over the value due to the direct binary-interaction between hydrogen.

In this Letter we present a Monte Carlo (MC) simulation study on the screening potential between itinerant hydrogen in PdH and TiH₂, two of the typical metal hydrides used in "cold fusion" experiments. We shall thereby demonstrate that the periodic lattice potential of metal atoms, constructed consistently with observed behaviors¹⁰ of hydrogen in such metals, can modulate the local density to an extent such that the fusion rate is enhanced greatly by more than ten orders of magnitude at room temperatures. We then perform MC simulation of itinerant hydrogen in lattice with *defects* to find a drastic modification further on the short-range correlation, which may

bring the fusion rate to an observable range. We shall caution, however, that these predictions on the fusion rate are extremely sensitive to fine structures in the adopted local fields.

The MC method has provided the most accurate data on screening potentials in one-component plasmas^{6,8} and in binary-ionic mixtures,¹¹ used for the calculation of reaction rates in dense stellar matter. The itinerant hydrogen in metal differs from that in dense stellar matter in two important aspects: Hydrogen in metal hydride is strongly screened by valence electrons and by nearly localized electrons in hybridized states.⁹ Microscopic inhomogeneity stemming from periodic or aperiodic (due to defects) lattice fields may drastically alter the features in short-range correlation between hydrogen. It is the purpose of this work to elucidate the latter aspect in detail.

The potential $V(r)$ of binary interaction between hydrogen was calculated⁹ in terms of the charge-form factors derived from the s-d hybridized electrons and by taking account of the dielectric screening due to valence electrons. The result was parametrized for the repulsive and attractive parts as

$$V_R(r) = (e^2/\epsilon_c r) [\exp(-r/D_S) + (r/r_R)^p \exp(-r/D_R)], \quad (2)$$

$$V_A(r) = - (e^2/\epsilon_c r) (r/r_A)^q \exp(-r/D_A) \quad (3)$$

where $V(r) = V_R(r) + V_A(r)$. We estimated⁹ the core-electron dielectric constant $\epsilon_c = 1.25$ for Pd and 1.36 for Ti, and found⁹ for PdH (TiH₂) $D_S = 0.19 \text{ \AA}$ (0.28 \AA), $p = 8.9$ (10.0), $r_R = 1.04 \text{ \AA}$ (1.00 \AA), $D_R = 0.18 \text{ \AA}$ (0.17 \AA), $q = 2.7$ (2.9), $r_A = 0.74 \text{ \AA}$ (0.61 \AA), and $D_A = 0.23 \text{ \AA}$ (0.25 \AA).

The rate of fusion per a pair of a and b with the binary interaction $V(r)$ is then calculated approximately as⁹

$$\lambda_{ab}^0 \simeq 10^{10} S_{ab}(\text{keV } b) P_{ab} / [M_{ab}(\text{amu})T(\text{K})]^{1/2} \quad (\text{s}^{-1}).$$

Here we have taken the larger of n_a and n_b to be $6 \times 10^{22} \text{ cm}^{-3}$. The Gamow penetration factor P_{ab} at room temperatures is given by

$$P_{ab} = \exp\left\{-\frac{2}{\hbar} \int_0^{r_1} dr [2M_{ab} V(r)]^{1/2}\right\} \quad (4)$$

where M_{ab} is the reduced mass, and r_1 is the radius at which $V(r)$ first vanishes;⁹ $r_1 = 0.62 \text{ \AA}$ in PdH and 0.69 \AA in TiH₂. Assuming $T = 300 \text{ K}$, we obtained⁹ $\lambda_{ad}^0 = 2 \times 10^{-53} \text{ s}^{-1}$ in PdH and $3 \times 10^{-58} \text{ s}^{-1}$ in TiH₂.

Values of the reaction rates λ_{ab}^0 depend sensitively on the binary potential $V(r)$. The attractive part, Eq. (3), has lowered the short-range part of the potential and thereby reduced r_1 , leading to a significant enhancement of fusion rate over that between unscreened hydrogen. Yet the values of λ_{ad}^0 cited above are far below an observable level, which we arbitrarily take as $\lambda_{ab} > 10^{-25} \text{ s}^{-1}$. It appears impossible to bring λ_{ab}^0 into such a range through whatever reasonable modification one might make on $V(r)$.

The statistical-mechanical enhancement factor $\exp[\beta H_{ab}(0)]$ should thus play an essential part in metal hydrides as in the supernova mechanism of white dwarfs.⁶ To analyze, we split the screening potential into the repulsive and attractive parts: $H_{ab}(r) = H_R(r) + H_A(r)$, as in $V(r)$. A quantum-mechanical treatment of the attractive part through a consideration of quasi-bound pairs at the potential trough of Eq. (3) showed,⁹ however, $\exp[\beta H_A(0)] \simeq 1$.

The major contribution to $H_R(r)$ comes from cumulative scattering through the second, long-range part of Eq. (2), the range of which extends over nearest-neighbor distances of hydrogen; hence, the classical approximation,^{9,12}

$$H_R(r) = V_R(r) + \ln[g_R(r)]/\beta, \quad (5)$$

can be used for its evaluation. We are led to perform MC simulation in a *fictitious* system of particles interacting via $V_R(r)$ for the calculation of $g_R(r)$; $H_R(r)$ is then obtained in accord with Eq. (5).

The lattice fields for itinerant hydrogen are constructed so that the following observed features may be taken into account: In densely hydrated phases, both Pd and Ti assume a *fcc* structure with lattice constants, $d = 4 \text{ \AA}$ and 4.4 \AA , respectively. In Pd lattice,^{10,13} hydrogen sits around the octahedral(O) sites where the potential assumes local minima with curvature $\sim 1.1 \text{ eV \AA}^{-2}$; barrier height between the minima is $\sim 0.23 \text{ eV}$ inferred from diffusivity. In Ti lattice,^{10,14} the tetrahedral(T) sites are the local minima with curvature $\sim 5.1 \text{ eV \AA}^{-2}$ and barrier height $\sim 0.51 \text{ eV}$.

For a construction of Pd fields with the features mentioned above, we found it *sufficient* to use a single-term expression,

$$V_{\text{Pd-H}}(r) = [22.2(\text{eV \AA})/r] \exp[-r/0.42(\text{\AA})] . \quad (6)$$

For Ti fields, on the other hand, we found it necessary to add a long-range repulsive term, to suppress occupation at octahedral sites, so that

$$V_{\text{Ti-H}}(r) = [31.8(\text{eV \AA})/r] \{ \exp[-r/0.51(\text{\AA})] + [r/1.095(\text{\AA})]^{10.57} \exp[-r/0.23(\text{\AA})] \} . \quad (7)$$

The equipotential contours on the {110} plane so calculated for Pd and Ti fcc lattices with and without missing atoms (defects) are portrayed in Figs. 1 and 2. As expected, broad potential minima appear around a defect, which may trap one or more hydrogen atoms.

Periodic lattice fields for the MC simulation are obtained by placing 500 metal atoms at fcc sites in a MC cell with periodic boundary conditions. Fields with defects are produced by removing 8 metal atoms randomly in such a way that no pairs of defects occupy nearest neighbor positions. The corresponding numbers, 500 for PdH and 1,000 for TiH₂, of hydrogen atoms are placed in the cell at random. A sequence of MC configurations are then generated through the random displacements of hydrogen positions, in the Metropolis algorithm¹⁵ with the canonical distribution for the sum of interaction energies between metal

and hydrogen and between hydrogen atoms. Several runs of such simulations have been performed to cover various cases of metal hydrides at temperatures: 1,200, 600, 300, and 200 K. Each run consisted typically of $(1-3) \times 10^4$ configurations per hydrogen atom (c/M_H), to assure thermalization of the system.

Figures 3 and 4 show projection maps of particle positions onto a $\{110\}$ plane, located within a slab of width $2^{-3/2} d$ centered at the $\{110\}$ plane. The particle positions are plotted at an interval of $c/M_H = 2 \times 10^3$ configurations, from solid circles to open circles, over a total interval of 6×10^3 configurations. More "motions" of particles are seen at $T = 600$ K than at $T = 300$ K. Although the MC particles appear almost frozen at the O-sites in Pd and at the T-sites in Ti for $T \lesssim 300$ K, they are still itinerant in that the mean square displacements $\langle \Delta r^2 \rangle$ of positions are found proportional to c ; the "coefficient of diffusion" $\langle \Delta r^2 \rangle / c$ is roughly proportional to $\exp(-\beta U)$, with the value of U close to the barrier height adopted for the lattice potentials. We also note in those figures that particles tend to coalesce around lattice defects. We remark parenthetically that those simulations were performed for a fictitious system of classical particles in a prescribed lattice field, with the purpose of finding out $H_R(r)$; Figs. 3 and 4 should not exactly correspond to the real behavior of hydrogen in metal hydrides.

The joint probability density $g_R(r)$ is calculated in the statistical ensemble of particle configurations generated by the simulation. As Figs. 5 and 6 illustrate, the resulting values of $H_R(r)$ in the "visible" short-range part can be fitted quite accurately by a functional form, $H_R(r) = A + B \exp(-Cr)$. Extrapolation of this fit to $r = 0$ would yield $H_R(0) = A + B$.

To examine the accuracy of the extrapolation scheme, we performed a control experiment by MC simulation, where the particles interacting via the repulsive potential (2) were distributed in the MC cell *without* the lattice fields. With the potential (2) appropriate to PdH, the extrapolated value $\beta H_R(0)$ of the simulation gave 2.86, while for the TiH₂ potential it was 9.48, both at $T = 300$ K. In such a homogeneous system of a known

potential, on the other hand, one can accurately evaluate $\beta H_R(0)$ from the solution to appropriate integral equations,^{8,9} to find $H_R(0) = 2.89$ (PdH) and 8.16 (TiH₂) at $T = 300$ K. We conclude that no corrections are necessary for the extrapolation of simulation data in the PdH potential while a reduction by 14% is required in the cases of TiH₂; $V_R(r)$ is more long-ranged⁹ in TiH₂ than in PdH. TABLE I summarizes the values of $\beta H_R(0)$ so obtained in various cases of metal hydrides.

The total rates of fusion, $\lambda_{ab} = \lambda_{ab}^0 \exp[\beta H_{ab}(0)] \simeq \lambda_{ab}^0 \exp[\beta H_R(0)]$, now exhibit a steep increase with β , a usual characteristic of a statistical-mechanical effect. At $T = 300$ K, the periodic lattice fields are found to raise the fusion rate over the homogeneous cases by a factor of 3×10^{10} in PdH and 7×10^{20} in TiH₂, resulting in $\lambda_{aa} \simeq 10^{-41} \text{ s}^{-1}$ (PdH) and 10^{-33} s^{-1} (TiH₂).

When the periodic lattice fields are perturbed by defects, the enhancement factor from TABLE I increases drastically in TiH₂ while it rather decreases in PdH. Since Eq. (7) has an extra term of long-range repulsion as compared with Eq. (6), the potential fields around defects in TiH₂ have much finer structures with microscopic undulation than those in PdH. As seen in Fig. 6, the resulting short-range modulation of density is the cause of the enhancement. The value in TABLE I implies $\lambda_{aa} \simeq 7 \times 10^{-23} \text{ s}^{-1}$ for TiH₂ with defects at $T = 300$ K. Possibility of such an "observable" fusion rate thus depends extremely sensitively on microscopic details in lattice fields, corroborating qualitatively the varied results in recent experiments.¹⁻⁵

We remark that the simple potential of Eq. (6) adopted for Pd tends to produce rather a monotonous field distribution around a defect, which may bring the short-range correlations in hydrogen more toward those in homogeneous cases, and hence reduction in enhancement. The potential (6), though sufficient to reproduce experimental features in the lattice fields, may be subject to modification, since the large number of nearly localized outer-shell d-electrons may generally induce a long-

range repulsive part for Pd, as Eq. (2) illustrates. If this is the case, defects in PdH may likewise act to enhance the fusion rate.

Finally we note in TABLE I an incredibly large reaction rate predicted for TiH₂ with defects at T = 200 K. At such a low temperature, however, quantum-mechanical effects should significantly modify the short-range correlations with the repulsive forces under consideration. To elucidate low-temperature effects, one must therefore proceed to consider quantum-statistical simulations of hydrogen in lattice with the interaction potentials fully taken into account. Since the principal quantity under study, $g_{ab}(0)$, is infinitesimally small in magnitude, an ultimate accuracy is called for in such a simulation, a challenge by itself for theoretical physics.

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FIGURE CAPTIONS

- FIG. 1 Equipotential contours for hydrogen in eV on the {110} plane of fcc Pd lattices. Zero level is at the O-sites (with dark shadow) in a periodic lattice (left); potential in a lattice with defect is on the right.
- FIG. 2 Same as Fig. 1, but for fcc Ti lattices. Zero level is at the T-sites.
- FIG. 3 MC displacements of hydrogen in Pd lattices (open squares). Left, periodic lattice; right, lattice with defect; top, $T = 600$ K; bottom, $T = 300$ K.
- FIG. 4 Same as Fig. 3, but in Ti lattices.
- FIG. 5 Repulsive screening potentials between hydrogen in Pd and their short-range fitting by the formula: $A + B \exp(-Cr)$. Solid circles and lines, periodic lattice; open circles and dashed lines, lattice with defect.
- FIG. 6 Same as Fig. 5, but in Ti.

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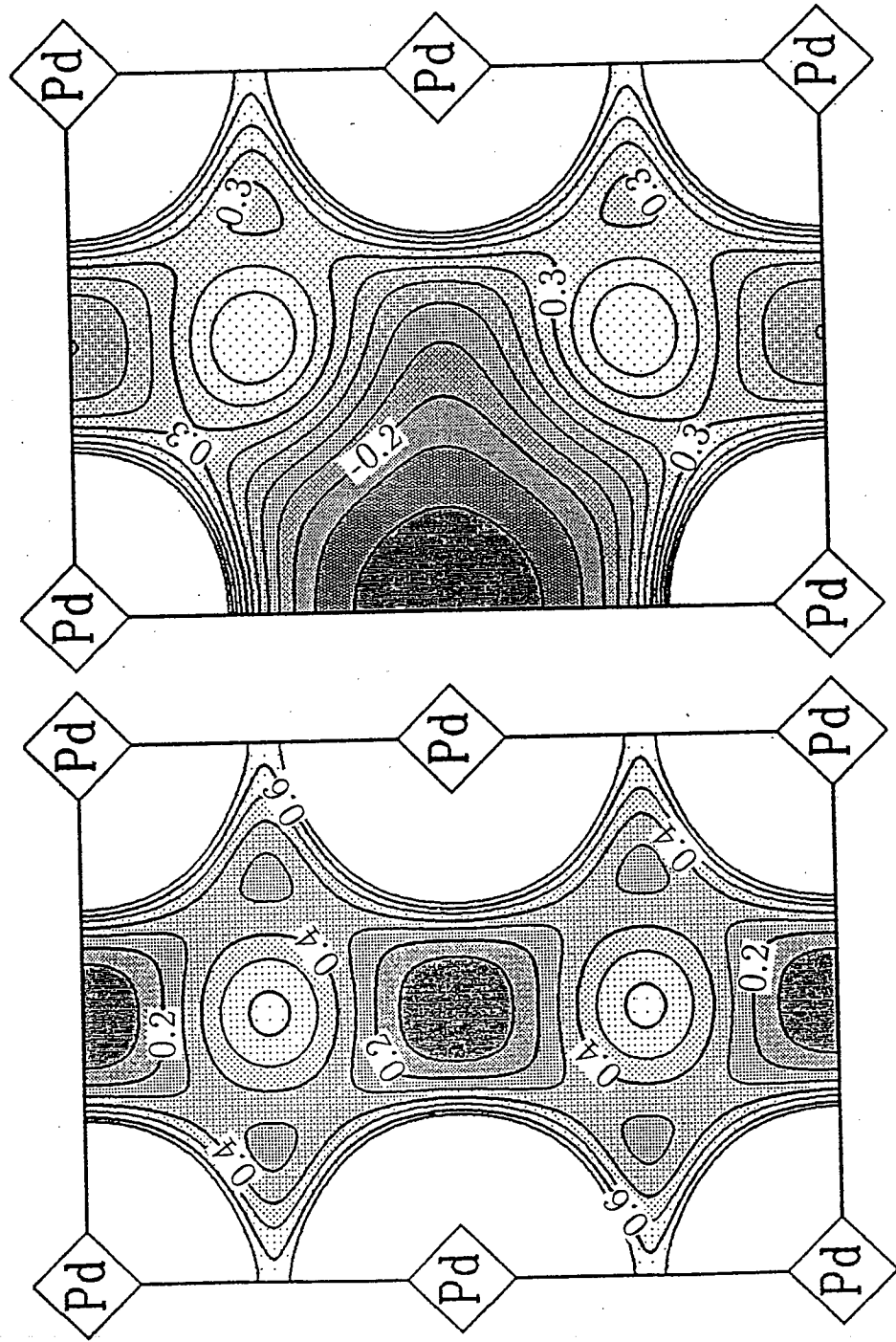


FIG. 1 Ichimaru et al.

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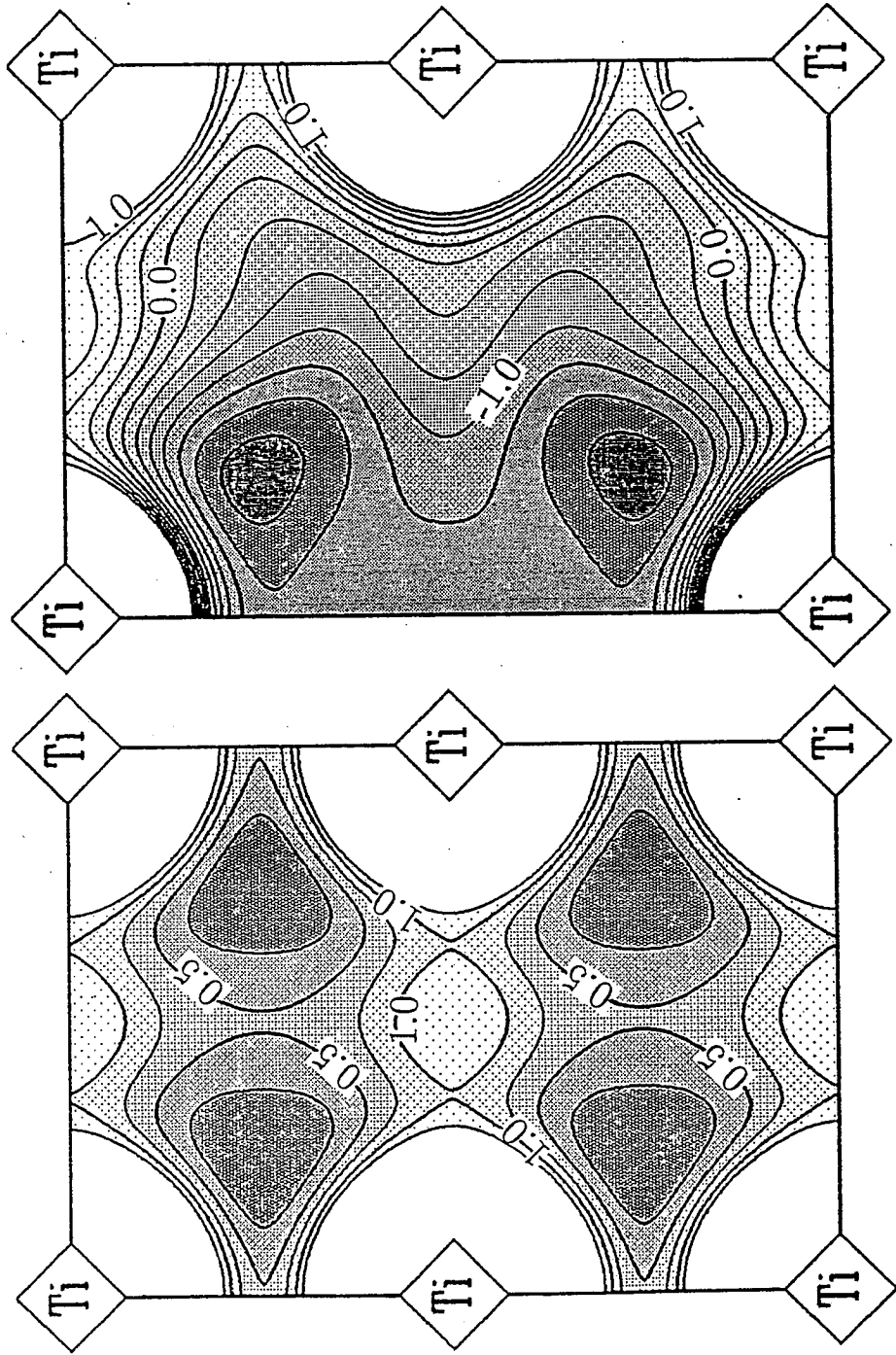


FIG. 2 Ichimaru et al.

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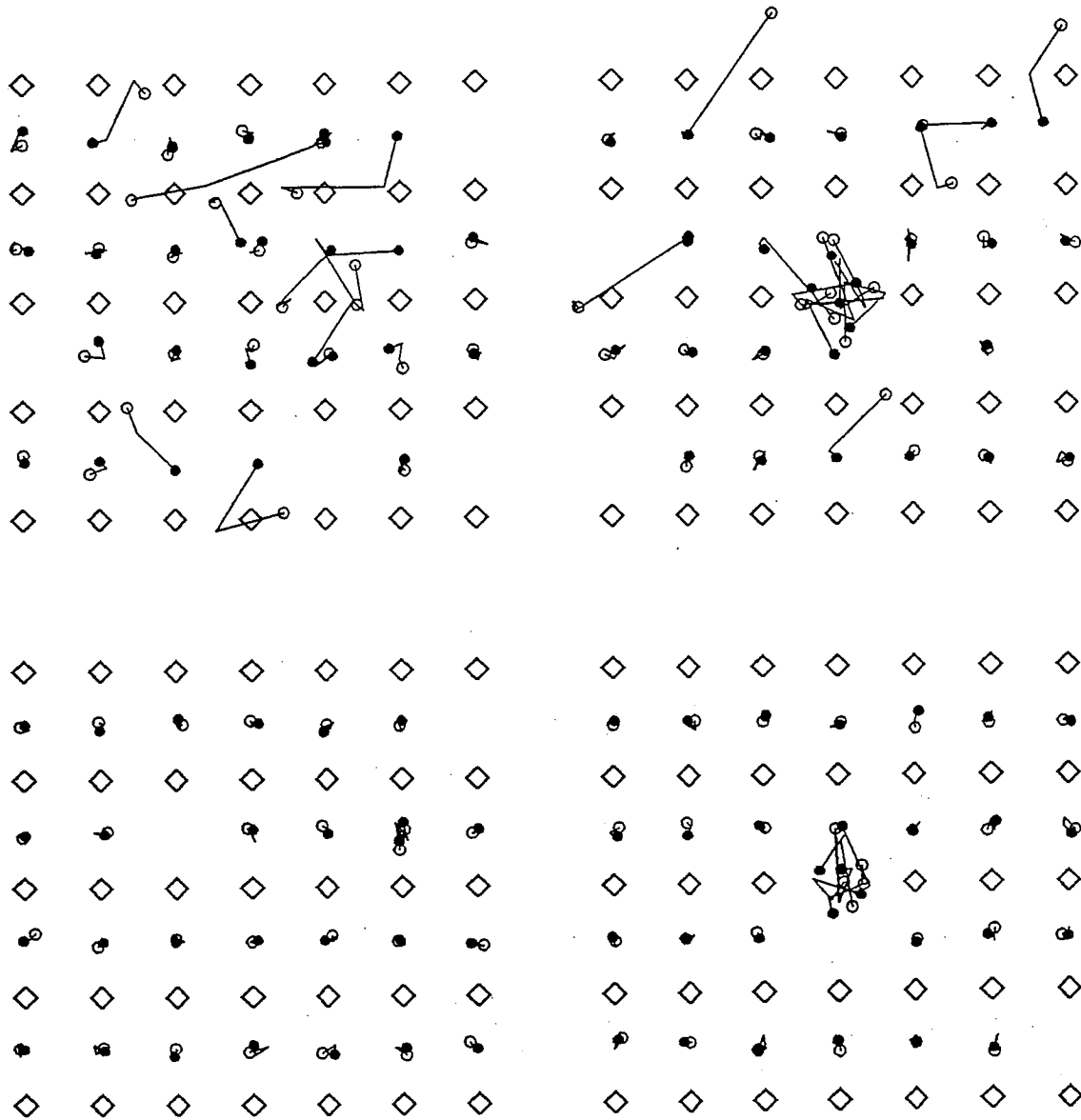


FIG. 3 Ichimaru et al.

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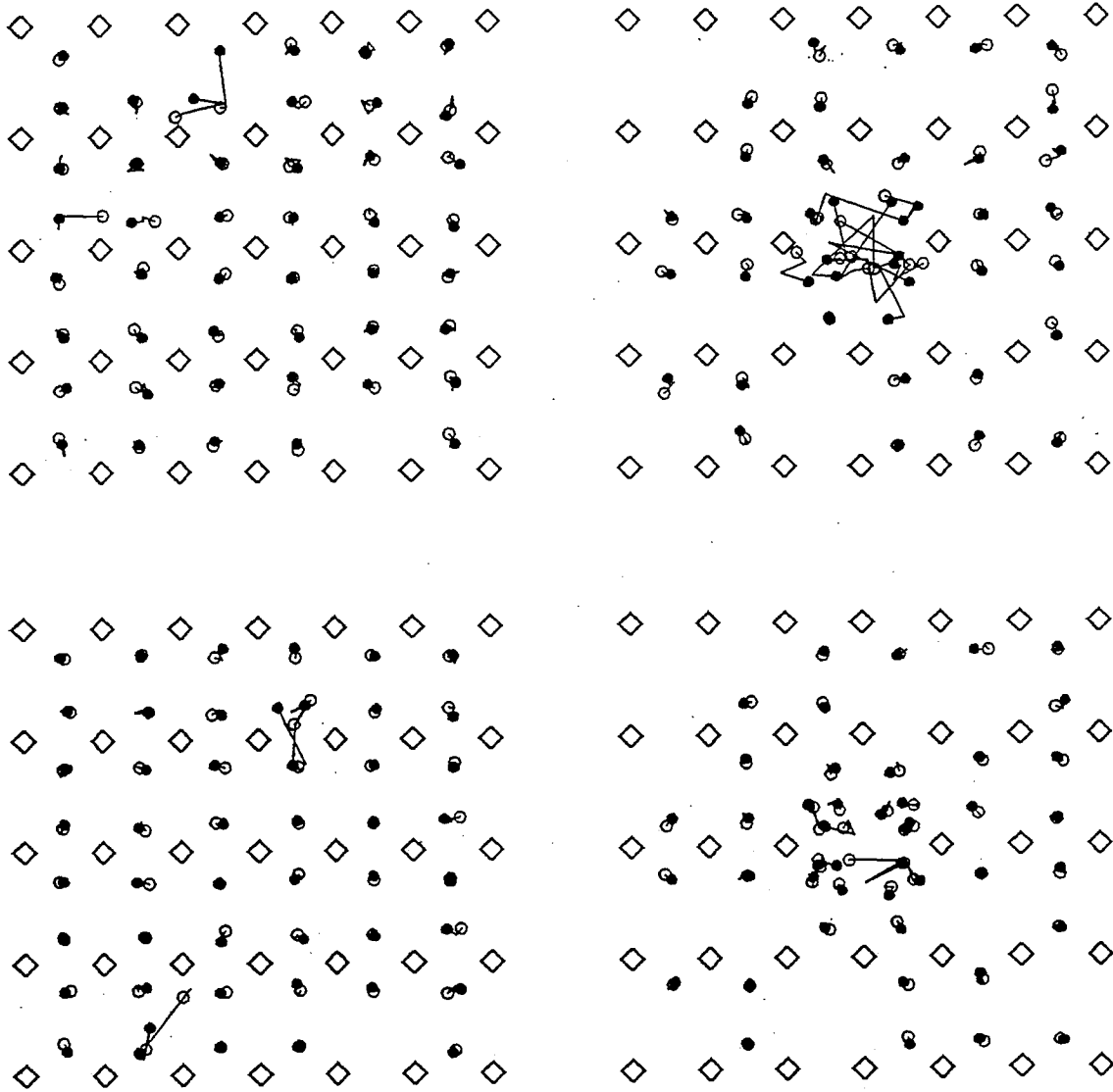


FIG. 4 Ichimaru et al.

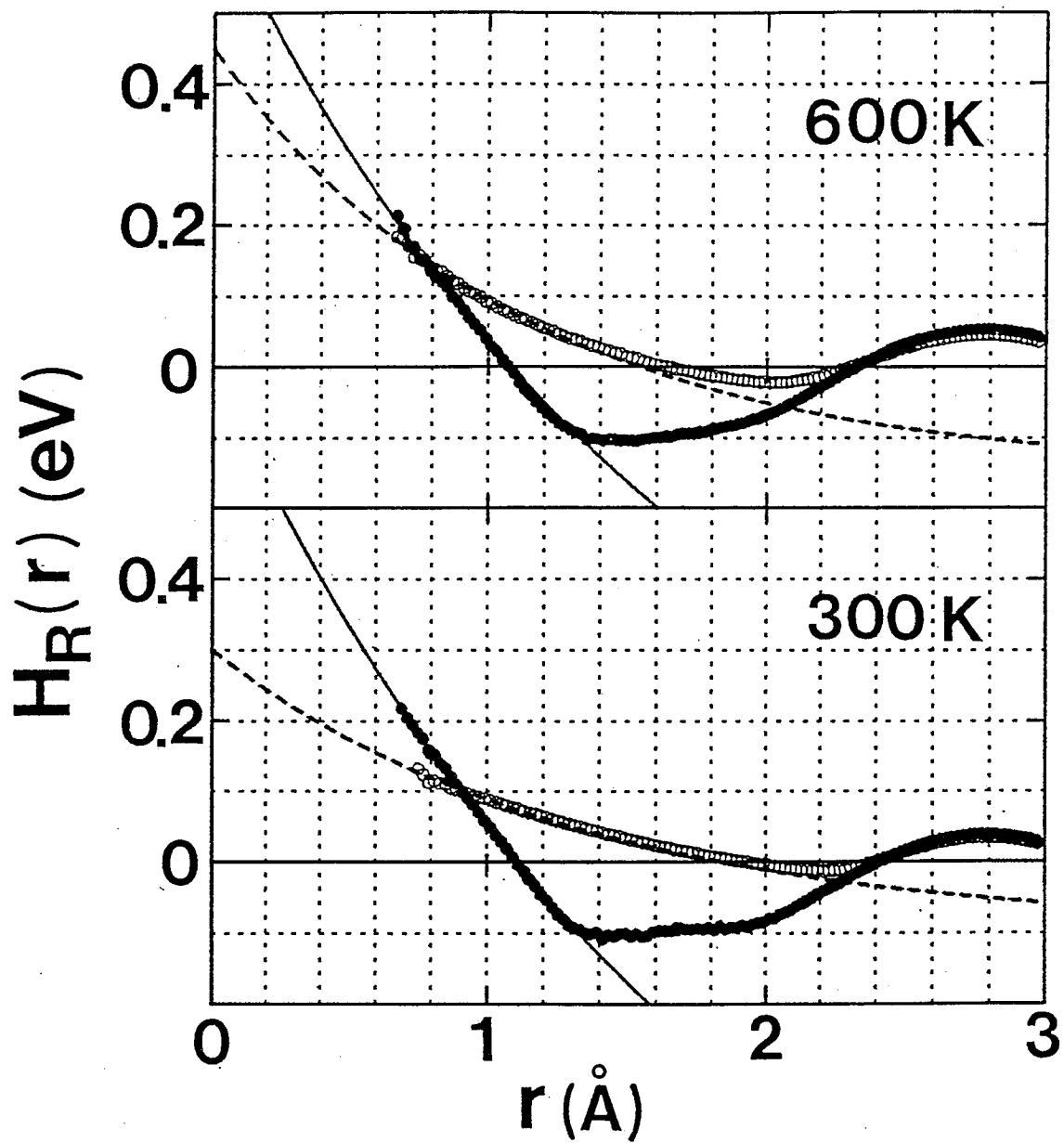


FIG. 5 Ichimaru et al.

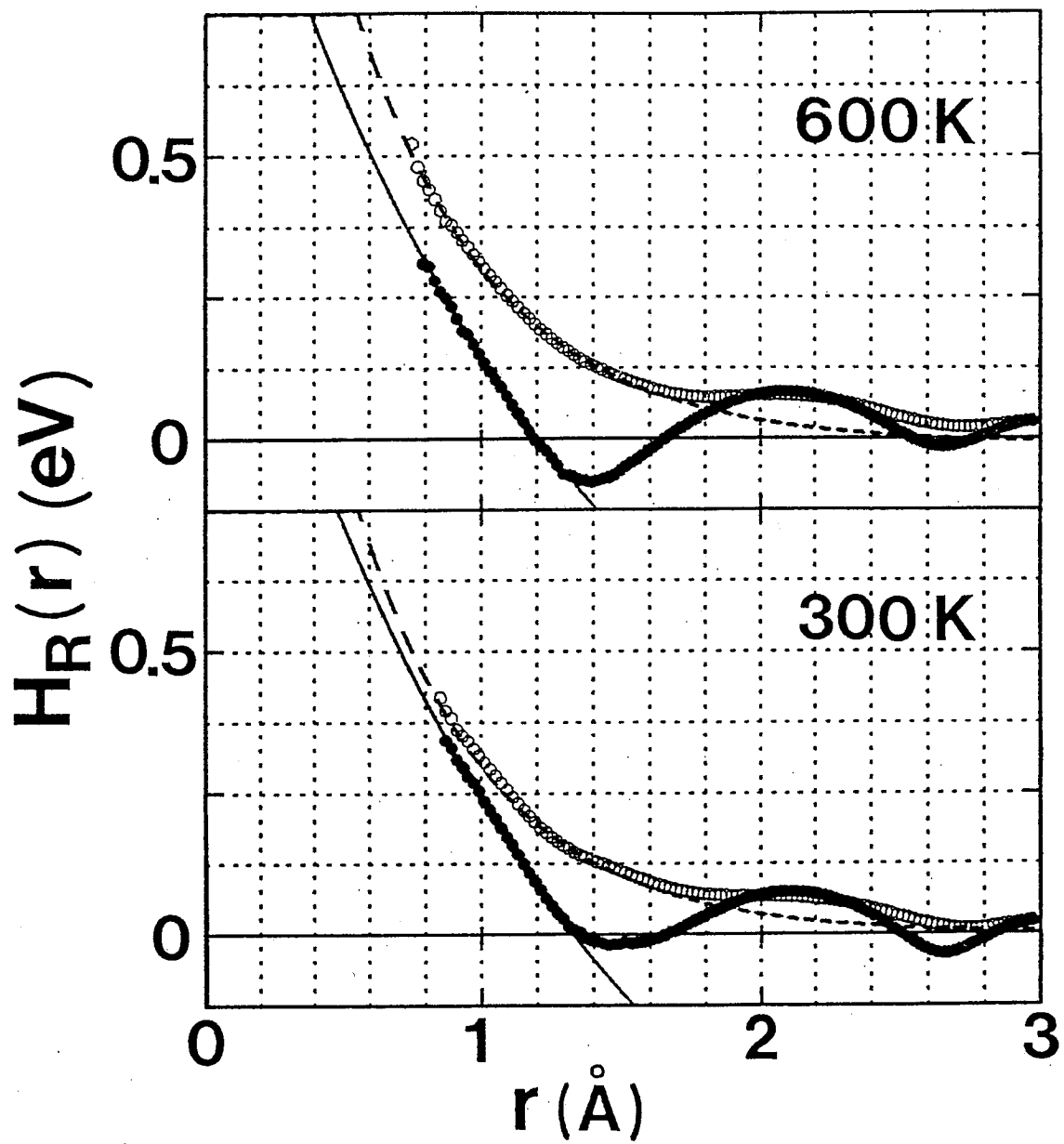


FIG. 6 Ichimaru et al.