# Fermi-surface imaging effect in the D short-range order of $PdD_x$

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A Fermi-surface imaging effect is proposed to explain the concentration-dependent D short-range order in the vicinity of the $(1,\frac{1}{2},0)$ point of $PdD_x$ with $0.7 < x < 0.78$. Within a rigid-band approximation the shape of the Fermi surface in $PdD_{0.75}$ is deduced from that calculated by Gupta and Freeman for stoichiometric PdH. In $PdD_{0.75}$ the obtained Fermi surface shows flat portions and $2k_F$ vectors close to the $(1,\frac{1}{2},0)$ points.

## I. INTRODUCTION

The phase diagram of the palladium-hydrogen system $[PdH_x(D_x)]$ had to be extended at low temperatures since the recent discovery of interstitially ordered D structures. By neutron scattering techniques the ordering of D atoms, located on their octahedral interstitial sites, has been found to occur on (420) lattice planes for concentrations from $x=0.63$ to 0.78.[1-4] This ordering is concentration dependent and occurs within the temperature region of the known "50-K anomaly" of specific heat.[2]

At lower concentrations for $x$ from 0.63 to 0.69 a superlattice reflection appears at the $(1,\frac{1}{2},0)$ point, indicating the presence of an interstitial $I4_1/amd$ structure (Ni-Mo type) with two subsequent (420) planes filled with D atoms and two vacant planes.[3,5] At higher concentrations for $x > 0.76$ a superlattice reflection forms at the $(\frac{4}{5},\frac{2}{5},0)$ point showing the nucleation of an $(I_4/m)$ structure ($Ni_4$-Mo type), with four (420) planes filled and one vacant.[1] At the intermediate concentrations, however, no long-range order appears but the short-range order present already above the transition temperature ($T_c$) remains unchanged even after long annealing times.[2,6] Moreover, the short-range order intensity present above $T_c$ is strongly concentration dependent, i.e., it shows for lower concentrations ($x < 0.69$) a diffuse intensity distribution well centered at the $(1,\frac{1}{2},0)$ point but exhibits for $0.70 < x \leq 0.78$ complicated isointensity contours with maxima outside the $(1,\frac{1}{2},0)$ point, e.g., in $PdD_{0.75}$ a broad maximum is found at (1.15,0.5,0). Furthermore, the broad satellite peaks approach the $(1,\frac{1}{2},0)$ point[2] with decreasing concentration.

The ordering on (420) planes in fcc lattices has generally been discussed by de Fontaine[7] in terms of a harmonic approximation of the free energy leading to the "special point" concept for ordering waves which predicts, for the short-range ordered state above the transition temperature for the whole (420) series (i.e., the different $Ni_n$-Mo structures), a short-range order intensity well centered at the $(1,\frac{1}{2},0)$ point. The theoretical expectations on the occurrence of the short-range order uniquely at special points are clearly not obeyed by the experimental results in the $PdD_x$ system. In the present communication we have tried, therefore, to analyze the discrepancy of the short-range order behavior in $PdD_x$ with the special point concept and also the Clapp-Moss theory.[8] In view of this analysis based on a rigid-band approximation of the Fermi surface for nonstoichiometric $PdD_x$ we propose a Fermi-surface-imaging effect in the short-range order to account for the experimental situation.

## II. ANALYSIS OF THE SHORT-RANGE ORDER BEHAVIOR

The short-range ordered state leading to the complicated concentration-dependent intensity distribution in the vicinity of the $(1,\frac{1}{2},0)$ point, for $x$ from 0.71 to 0.78 has structurally been described in two recent papers[5,9] by the occurrence of "mixed domains" consisting of cells of the $Ni_n$-Mo type. The region in the phase diagram where this short-range order appears is shown in Fig. 1. In the framework of this "mixed domain" concept the observed intensity distribution is due to an average over an ensemble of unit cells of the different $Ni_n$-Mo structures put together like mosaic stones. The observed experimental results could be reproduced if furthermore a distortion of the D atom towards the vacant site was taken into account. Furthermore, it was argued that the occurrence of the mixed structure was favored by the near degeneracy of the energy of the composing $Ni_n$-Mo cells leading to frustration effects at low temperatures.

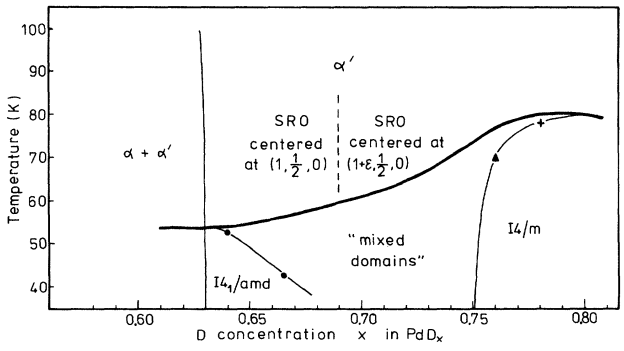


FIG. 1. Schematic view of the different structural states occurring in $PdD_x$ at low temperatures. The dotted line shows approximately the boundary between the different short-range order patterns. The thick full line shows the locus of the 50-K anomaly. The points denoted by the symbols (●), (▲) and (+) show experimental phase boundary results from Refs. 11, 1, and 2, respectively.

 

These arguments, however, which may explain the nonoccurrence of the long-range ordered structure at intermediate concentrations are no longer applicable at higher temperatures, where the system is rather in thermodynamic equilibrium. Recent neutron scattering measurements have indeed shown that the shape of the complicated isointensity contours remain essentially the same even up to 200 K, where the diffuse intensity has decreased to about $\frac{1}{10}$ of its maximum value.[10] Therefore, the discrepancy between the experimental results for the short-range order in $PdD_x$ for $0.71 \leq x \leq 0.78$ and predictions of a "special point" short-range ordering still exists for higher temperatures.

Alternatively, in the lower-concentration range the diffuse intensity pattern with a maximum centered at the "special point" $(1,\frac{1}{2},0)$ may easily be described within the Clapp-Moss theory for first ($V_1$) and second neighbor ($V_2$) interactions with a ratio $0 < V_2/V_1 < 0.5$. However, even with concentration-dependent $V_1$ and $V_2$ the Clapp-Moss theory is not able to explain the transition to the split distribution at higher concentrations.[8]

Moreover, a recent Monte-Carlo simulation, taking into account also second-neighbor interactions, could only explain the experimental results in the low-concentration range.[11]

## III. FERMI-SURFACE MECHANISM

The occurrence of intensity maxima near but outside the $(1,\frac{1}{2},0)$ point in the diffuse intensity above $T_c$ indicates the presence of secondary minima in the $K$-space potential $V(K)$ near the $(1,\frac{1}{2},0)$ special point minimum for the concentration range $0.71 < x < 0.78$ in $PdD_x$. The failure of the Clapp-Moss theory with first- and second-neighbor interactions, furthermore, suggest a description in terms of higher-order interactions.

It is well known that long-range interactions may arise from Fermi-surface porperties, i.e., the occurrence of flat portions in the Fermi-surface geometry. Diffuse satellites near the (1,1,0) point have first been related for $Cu_3Au$[12] and more recently for transition-metal alloys[13] to wave vectors connecting flat portions of the Fermi surface. It has been noted that the flattening of the Fermi surface, calculated recently for $Cu_xPd_{1-x}$ (Ref. 13) is a strong phenomenon in these alloys as the Fermi surface must evolve continuously from the concave shape in the transition metal into the convex one in the noble metal.

The $PdD_x$ system is electronically similar to transition noble metal alloys and, consequently, a similar flattening of the Fermi surface should occur in a certain concentration range. Figure 2 shows the Fermi surface of stoichiometric PdH as calculated by Gupta and Freeman[14] and depicts a deformed sphere with flatter portions perpendicular to the [110] direction. To obtain the Fermi surface for $x = 0.75$ of $PdD_x$, i.e., for the cencentration region where the experimental effects which we want to explain occur, a rigid-band approximation was used. Assuming that the Fermi level $E_F$ lies, for $x$, 0.65 near the top of the Pd $d$ bands, in accordance with several calculations and experimental results,[15] and taking for the slowly varying density of states above the Pd $d$ states a constant value, one can deduce from the band calculations in stoichiometric PdH the Fermi energy for a $PdD_{0.75}$ system. From the band calculations one further obtains the corresponding Fermi vectors in the main symmetry directions.

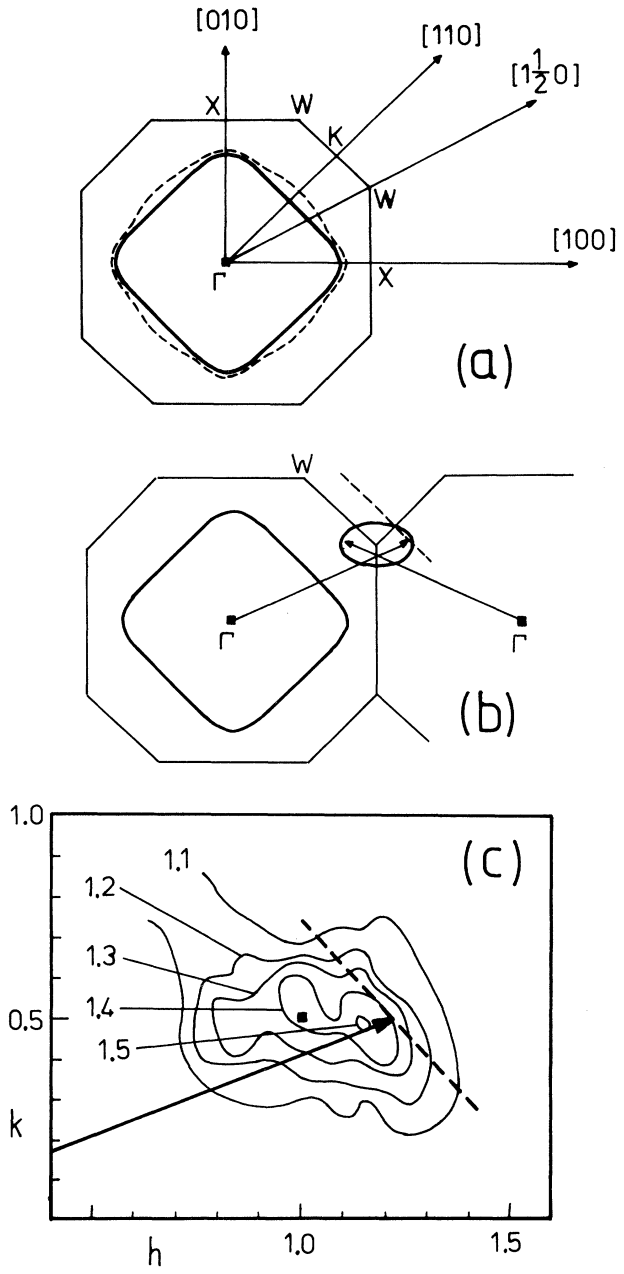


FIG. 2. (a) The Fermi surface for $PdD_x$. The dotted line shows the calculated contour for stoichiometric PdD by Gupta and Freeman (Ref. 14). The solid line shows the Fermi contour with flat portions in $PdD_{0.75}$ obtained from a rigid-band approximation. (b) The $2K_F$ mechanism in the vicinity of the special point $(1,\frac{1}{2},0)$. The ellipsoid arround the $W$ point indicates the width of the special point minimum of $V(k)$. The arrows show $2K_F$ vectors from the first Brillouin zone. (c) The $2K_F$ mecahnism and the experimental contours in $PdD_{0.75}$. The arrow indicates a $2K_F$ vector and the dotted line the loci of $2K_F$ vectors.

This rigid-band approach yields for $PdD_{0.75}$ a value for $E_F = 0.56$ Ry and a Fermi surface shown by the solid line in Fig. 2(a). As in the band structure of PdD the energy versus $K$ relation is much steeper in the $\Gamma x$ direction ([100]

direction) than in the $\Gamma k$ direction ([110] direction) the Fermi surface has become flatter when the concentration was decreased to $x=0.75$.

In Fig. 2(b) $2K_F$ vectors for $PdD_{0.75}$ are shown pointing in the vicinity of the $(1,\frac{1}{2},0)$ point. The $2K_F$ vectors from the flat portion of the Fermi surface describe a line in Fig. 2(b) which approaches the $(1,\frac{1}{2},0)$ region. A $2K_F$-induced local minimum of $V(K)$ in principle is induced along the whole line, but only when the line approaches the vicinity of a special point, i.e., the $(1,\frac{1}{2},0)$ in the present case the $2K_F$ minimum should influence the ordering process. In the vicinity of the $(1,\frac{1}{2},0)$ special point, where the $K$-space potential $V(K)$ shows a broad absolute minimum the superposition of a $2K_F$-induced minimum may create a resulting $V(K)$ in the neighborhood of the $(1,\frac{1}{2},0)$ with secondary minima outside the $(1,\frac{1}{2},0)$ point. (A local $2K_F$-induced minimum far away from an absolute minimum is energetically unfavorable and should not influence the ordering process.)

The width of the "special point" minimum can be obtained from neutron scattering results in $PdD_{0.69}$,[5] where the short-range order peak is relatively well centered at the $(1,\frac{1}{2},0)$. The ellipsoid around the $W$ point in Fig. 2(b) shows the full-width-half-maximum contour of the diffuse intensity in $PdD_{0.69}$ reflecting the extension of the special point minimum around $(1,\frac{1}{2},0)$ and shows the intersection of the $2K_F$ lines with the longer main axis of the ellipsoid at (1.2,0.5,0) and (0.8,0.5,0) points, respectively.

Moreover, a further decrease of the D concentration reduces the Fermi vectors, so that they approach the $(1,\frac{1}{2},0)$ point and inducing, therefore, the concentration-dependent short-range order experimentally observed.

## IV. DISCUSSION

The experimentally observed intensity pattern in $PdD_{0.75}$ shows a broad diffuse peak with a full-width-half-maximum contour extending towards a (1.25,0.5,0) point with a maximal intensity located near a (1.15,0.5,0) position. The present Fermi-surface effect, leads to $2K_F$ vectors pointing in the vicinity of the $(1,\frac{1}{2},0)$ point, i.e., near a (1.2,0.5,0) position Fig. 2(c). This position should be shifted somewhat further towards the $(1,\frac{1}{2},0)$ point because of the superposition of a broad intensity around the $(1,\frac{1}{2},0)$ with the intensity of the satellite peak and should therefore approach the experimental value.

The $2K_F$-imaging effect, proposed to explain the presence of secondary minima in $V(K)$ around $(1,\frac{1}{2},0)$ and derived from rigid band considerations ties together and explains the following findings:

(a) the split intensity pattern of short-range order even at higher temperatures;

(b) the concentration dependence of the satellite positions;

(c) further, it lifts the discrepancy with the special point ordering concept at the $(1,\frac{1}{2},0)$ point by introducing a long wavelength modulation of the $(1,\frac{1}{2},0)$ ordering wave;

(d) the $2K_F$ mechanism is further in agreement with recent results in a $Pd_{1-y}Ag_yD_x$ system, with small Ag concentration, indicating a scaling of the shape of the intensity distribution with the electronic concentration, i.e., with the Fermi-surface dimension.[16]

Finally, the Fermi-surface imaging effect gives also some insight in the structural description of the observed short-range order state by an ensemble of complex mixed structures. The $2K_F$ mechanism corresponds in real space to a modulation of the crystal potential by a Friedel-type oscillation inducing, therefore, long-range interactions between deuterons. These long-range interactions may stabilize the complex mixed structure. A ground-state calculation for fcc alloys by Kanamori and Kakehashi[17] including fourth-neighbor intractions revealed indeed complex structures similar to that found in Ref. (5) as fcc ground states.

## ACKNOWLEDGMENTS

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