EPR investigation of the phase diagram, of the electronic properties, and of the indirect exchange interaction in the PdGdH system

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Electron paramagnetic resonance was used to investigate a Pd–H system doped with small amounts of gadolinium. The limits of the phase diagram of the Pd–H states are established. It is found that the limits of the region of coexistence of the α and β phases correspond to the respective composition ratios H/Pd $= 0.07 \pm 0.02$ and 0.62 ± 0.02 at 20°C and 0.25 ± 0.02 and 0.55 ± 0.02 at 200°C. The effect of the electronic bottleneck was observed in the relaxation of the localized angular momenta of gadolinium in the β phase of the hydride. The exchange intergral of the interaction of the localized angular momenta of gadolinium and of the conduction electrons and the rate of the spin-lattice relaxation of the conduction electrons $\delta_{eL} = 6 \times 10^{11}$ sec^{-1}/at.% are determined. The effect of the electron-conduction mean free path on the indirect exchange interaction between the localized angular momenta of the gadolinium is investigated. It is found that the dependence of the magnetic-ordering temperature on the conduction-electron mean free path is described by an exponential function in accordance with the de Gennes theoretical calculations.

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INTRODUCTION

It is well known that the introduction of hydrogen into the crystal lattice of many metals leads to radical changes in their physical properties. A special place among the large class of compounds of hydrogen with metals is occupied by the hydrides of transition metals, particularly the hydrides of palladium and of alloys on its basis. The increased attention to the latter is due primarily to the observation of their superconductivity at sufficiently high hydrogen concentrations.

Palladium forms with hydrogen two phases, α and β, which differ substantially in their properties and have fcc lattices with constants that depend on the phase composition. The α phase, just as metallic palladium, is characterized by an unfilled d band with high state density of the conduction electrons on the Fermi surface, a fact that determines the anomalously high susceptibility of this phase, close to the susceptibility of ferromagnetic metals. The β phase, whose d band is completely filled, is diamagnetic because of the realignment of the electron structure, and at definite hydrogen concentrations it becomes a superconductor with sufficiently high critical temperature. The existence of α and β phases in a rather wide interval of hydrogen concentrations makes it possible to regard the Pd–H system as a model for the study of crystalline and electronic properties of compounds of metals with hydrogen, by smoothly varying these properties via changes in the hydrogen content of the sample.

The method of electron paramagnetic resonance has been successfully used of late to investigate the crystalline and electronic properties of metals. The method of EPR on localized magnetic states of an impurity introduced into the investigated substance as a probe can serve as a precise physical tool for the study of details of the electron spectrum, of the microstructure, and of various effects connected with the interaction of magnetic impurities. There are only few published communications devoted to EPR studies of the Pd–H system.[1,2] These studies were devoted to exchange interactions of localized magnetic moments of gadolinium and manganese introduced as impurities into palladium, on the one hand, and the conduction electrons, on the other. In the present paper we report the results of EPR investigations of the phase diagram of a palladium–hydrogen system doped with small amounts of gadolinium, the indirect exchange interactions between the spins of the gadolinium in the β phase of the palladium hydride, and present new data on the dynamics of the interaction of the spin systems of the localized moments of gadolinium and of conduction electrons. Preliminary results of the EPR measurements in Pd–Gd–H were reported by us earlier.[3]

EXPERIMENTAL PROCEDURE

The EPR measurements were made with a B-ER218S modulation spectrometer in the 3-cm band and in the temperature interval 1.6–30 K.

The samples were prepared in an arc furnace in an argon atmosphere, starting with palladium and gadolinium 99.9% pure each. The alloys obtained were cold rolled, and then annealed at 800 °C for 6 hours. The hydration of the Pd–Gd alloys was carried out by an electrolytic method in an aqueous solution of H_2SO_4 (0, 1N H_2SO_4) at a current density 25 mA/cm^2. The concentration of the hydrogen in the obtained samples was measured in units of the atomic ratio H/Pd. To obtain high hydrogen concentrations (up to H/Pd = 0.95) the sample was subjected to several hydration–dehydration cycles; the electrolysis was then performed in an alcohol solution of HCl at −78 °C and at a current density 10 mA/cm^2. Depending on the experimental conditions, the desorption of the hydrogen from the samples was carried out in Sieverts apparatus[4] in a vacuum of 10^{-5} Torr, or by the anti-electrolysis method.[5] The hydrogen content in the samples was determined after all the

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measurements by desorption of the hydrogen at 500 °C (during the intermediate stages of the measurement the hydrogen concentration was determined by weight). The accuracy in the determination of the composition in both cases was H/Pd = ±0.02. The samples for the measurements of the EPR were plates measuring 10 × 4 × 0.1 mm.

The amplitude measurements were performed relative to a signal from diphenylpicrylhydrazyl (DPPH), a small amount of which was placed in a resonator kept at room temperature.

The gadolinium concentration in the employed samples was 0.01 or 0.5 at.%.

EXPERIMENTAL RESULTS AND DISCUSSION

1. *Phase diagram.* Single absorption lines were observed in the EPR spectrum of the Gd^{3+} ions in samples with compositions H/Pd $\leq$ 0.03 and H/Pd $\geq$ 0.7, in fields corresponding to spectroscopic-splitting factors $g_1 = 1.81 \pm 0.01$ and $g_2 = 1.99 \pm 0.01$. In the intermediate region of the hydrogen concentrations, the EPR spectrum consisted of two well-separated EPR lines at the same values of the resonance fields (Fig. 1). It turned out that the temperature dependence of the widths of both lines could be represented at $T > 7$ K in the form of the relation $\Delta H = a + bT$. The coefficient b was independent of the gadolinium concentration and amounted to 6.3 Oe/K and 0.56 Oe/K for the lines with $g = 1.81$ and 1.99, respectively.

It is well known that in metals the shift of the g-factor and the width of the EPR line at localized magnetic states of the impurity are determined by the expressions (see, e.g., Ref. 6):

$$\Delta g = JN(E_F), \tag{1}$$

$$\Delta H = \frac{\pi}{g\mu_B}[JN(E_F)]^2 k_B T, \tag{2}$$

where J is the exchange integral of the interaction of the localized magnetic moments with the conduction electrons, and $N(E_F)$ is the state density of the conduction electrons on the Fermi surface. The existence in the Pd–H system of α and β phases with different conduction-electron state densities on the Fermi surface[7] makes it possible to identify unambiguously the resonance signals in the fields corresponding to $g = 1.81$ and 1.99 with the α and β phases of this system, respectively.

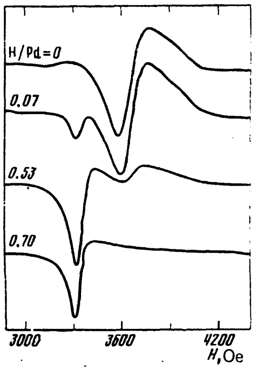

FIG. 1. EPR spectrum of 0.5 at.% Gd in the Pd-H system at 8 K.

Using the integrated intensity of the EPR lines corresponding to the α and β phases of the Pd–H system in the two-phase region as a measure of the volume content of each phase in the sample, we were able to investigate the boundaries of the two-phase region of the phase diagram for a number of samples obtained either electrolytically at 20 °C or by desorption of hydrogen from samples with composition H/Pd ~ 0.8 at 200 °C. Figure 2 shows the dependence of the integrated intensity of the resonance signals corresponding to the α and β phases on the hydrogen concentration in the samples obtained by electrolytic absorption and desorption of hydrogen at 20 °C. As seen from the figure, the obtained plots are well approximated by a linear function, this being a consequence of the validity of the "level rule" in the two-phase region.[8]

The exact values of the limiting compositions of the α and β phases were determined by extrapolating the two straight lines plotted by least squares to their intercepts with the H/Pd axis. It was found that the maximum hydrogen content at which an α phase still exists in the sample (α_{max}) corresponds to the composition with H/Pd = 0.62 ± 0.02, and the minimum-concentration limit of the existence of the β phase (β_{min}) corresponds to two values of H/Pd, 0.03 ± 0.02 and 0.07 ± 0.02, depending on whether the sample was obtained respectively by absorption or desorption of the hydrogen. This difference between the limits β_{min} of the phase diagrams for samples obtained by absorption and desorption of hydrogen observed earlier in investigations of the phase diagram of the Pd–H system by other methods.[8] In this case, as shown in Ref. 9, the equilibrium boundary of the two-phase region corresponds to the value H/Pd = 0.07 ± 0.02 determined from measurements on samples obtained by hydrogen desorption.

The validity of the "lever rule" for the integrated in-

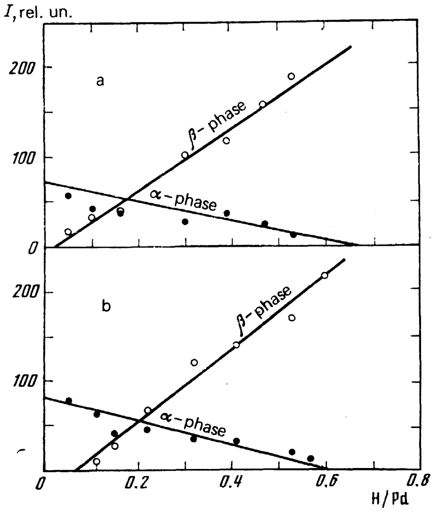

FIG. 2. Dependence of the intensity of the EPR signals corresponding to the α and β phases of the Pd-H system in the two-phase region, on the hydrogen concentration for samples obtained: a) by absorption and b) by desorption of hydrogen by an electrolytic method at 20°C.

tensities in the two-phase region enables us to determine the limiting compositions of the α and β phases from EPR measurements at only two hydrogen concentrations corresponding to the two-phase region. This procedure was used by us for samples obtained by desorption of hydrogen from samples with $H/P \approx 0.8$ at 200 °C. By connecting the ratio of the integral intensities corresponding to the α and β phases with the volume contents of each phase in the sample and by using the "lever rule," we found that the limit $\beta_{\min}$ corresponds to $H/Pd = 0.25 \pm 0.02$, while $\alpha_{\max}$ boundary corresponds to $H/Pd = 0.55 \pm 0.02$.

We have proposed earlier[3] that the values of the limiting compositions obtained in this manner correspond to the low-temperature phase diagram of the Pd–H system, since the EPR measurements were made at 8 K. However, the substantial difference between the limiting compositions obtained in the present study for samples produced at different temperatures allows us to conclude that when the samples are cooled to low temperatures for the EPR measurements they become quenched. This points likewise to good agreement of the experimental data obtained by us in measurements of samples prepared by the electrolytic method at 20 °C and by hydrogen desorption at 200 °C, on the one hand, with the results of the measurements of the pressure—temperature—composition curves[8] at the corresponding temperatures. Thus, the phase-diagram boundaries determined by us pertain to the temperatures at which the investigated samples were produced.

2. *Electronic properties of the α and β phases.* It is known that in metals, the localized magnetic moments of the impurity, on the one hand, and the conduction electrons, on the other, make up a spin system strongly coupled by exchange interaction, the rate of establishment of equilibrium in which is determined by the ratio of the relaxation rates of the conduction electrons relative to the lattice (δ_{eL}) and to the system of localized angular momenta (δ_{ei}).[10]

If the rate of the spin-lattice relaxation of the conduction electrons greatly exceeds the rate of the "inverse" relaxation of the conduction electrons relative to the spin system ($\delta_{eL} \gg \delta_{ei}$), then the width of the EPR line and the shift of the g-factor of the localized moments are determined in accordance with the Korringa relaxation mechanism by expressions (1) and (2).

At sufficiently high concentrations of the magnetic impurity, the rate of relaxation of the conduction electrons relative to the spin system can exceed the rate of the spin-lattice relaxation of the conduction electrons ($\delta_{ei} > \delta_{eL}$) and lead to the so-called electron bottleneck effect. In this case the width of the EPR line is determined by some effective relaxation time and the Korringa mechanism does not manifest itself in full measure. In order to discern the electron bottleneck effect in the relaxation of localized angular momenta one introduces into the system an additional nonmagnetic scatterer with strong spin–orbit coupling, thereby increasing the rate of the establishment of equilibrium of the conduction electrons with the lattice. At sufficient scatterer content, the temperature slope of the line width and the shift of the g-factor increase to the values determined by expressions (1) and (2).

The effect of the electron bottleneck in metals is frequently observed and makes it possible to determine from experiment the characteristic relaxation times of the conduction electrons and of the localized angular momenta, and in particular the time of the spin-lattice relaxation of the conduction electrons.

In the Pd–Gd–H system, the effect of the electron bottleneck was not observed up to now in either the α or β phase.[2]

1. *The α phase of Pd–H.* The absence of the electron bottleneck in the α phase can apparently be attributed to the fact that the d electrons, which determine the relaxation of the localized angular momenta of Gd in α-Pd–H have exceedingly short spin–lattice relaxation times. In this case the temperature slope of the EPR line width and the shift of the g-factor of the localized angular momenta are determined by the state density of the conduction electrons in accordance with expressions (1) and (2), since it can be assumed that the exchange integral remains constant within the limits of the α phase.

The character of the behavior of the temperature slope of the line width in the α phase with changing hydrogen concentration cannot be investigated in samples obtained by absorption and desorption of hydrogen by the electrolytic method at $T = 20$ °C, in view of the rather small values of the limit $\beta_{\min}$. Consequently an intense EPR signal from the β phase appears even at a small hydrogen content in the sample ($H/Pd \sim 0.03$). For samples obtained by hydrogen desorption at 200 °C, the dependence of the temperature slope of the EPR line width in the α phase is shown in Fig. 3. As seen from the figure, the temperature slope of the line width in the α phase has no simple dependence on the hydrogen concentration. The dependence of the temperature slope of the line width on the hydrogen concentration observed by us can be attributed to the "hard band" model based on the electronic structure of metallic palladium, is applicable only at low hydrogen concentrations ($H/Pd \approx 0.06$), when a monotonic decrease of $d\Delta H/dt$ takes place. It can be assumed that with further increase of the hydrogen content in the sample the changes of the lattice parameter that occur within the limits of the α phase lead to a substantial rearrangement of the band structure.

2. *The β phase of Pd–H.* Whereas in the α phase of the palladium hydride there is no electron bottleneck

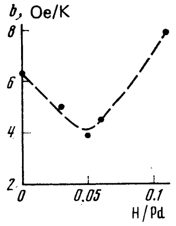

FIG. 3. Slope of EPR line, $b = d\Delta H/dT$ against the hydrogen concentration in the α phase for samples obtained by desorption of hydrogen at 200 °C.

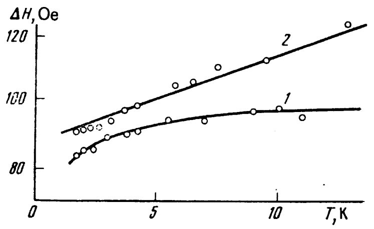

FIG. 4. Temperature dependence of the EPR line width for the following samples: 1) 0.01 at. % Gd in $PdH_{0.75}$, and 2) 0.01 at. % Gd + 0.25 at. % La in $PdH_{0.75}$.

because of the dominant role of the d electrons in the relaxation of the localized angular momenta of the gadolinium, in the β phase the d band turns out to be completely filled. The relaxation of the localized angular momenta should in this case be determined by the s-band electrons. The possibility of the electron bottleneck in the relaxation of localized angular momenta of gadolinium and manganese in Pd–H was already investigated in Ref. 2. This effect was not observed, however, for the localized angular momenta of gadolinium.

To investigate the feasibility of an electron bottleneck in the β phase of Pd–H, we performed measurements on samples containing 0.01 at. % Gd, in which the rate of relaxation of the conduction electrons was varied by adding a nonmagnetic impurity (scatterer) with strong spin–orbit coupling. The temperature dependence of the width of the resonance line for the investigated samples is shown in Fig. 4. It is clearly seen that introduction of 0.25 at. % lanthanum leads to an increase of the temperature slope of the line width, from 0.56 Oe/K without a scatterer to 2.3 Oe/K when lanthanum is introduced; this corresponds to opening up of the electron bottleneck in the relaxation of the localized angular momenta of the gadolinium and to realization of the Korringa relaxation mechanism (introduction of a large amount of lanthanum did not lead to a noticable increase of the temperature slope of the line width). We then obtained, in accordance with (2), $J = 0.034$ eV. For the state density of the conduction electrons on the Fermi surface we used the value $N(E_F) = 0.29\ \mathrm{eV}^{-1}\,\mathrm{spin}^{-1}\,\mathrm{atom}^{-1}$, as determined from measurements of the specific heat.[7]

For a sample without a scatterer, a nonlinear dependence of the line width on the temperature was observed in the region of low temperatures, (see Fig. 4). This behavior of the line width can occur under definite conditions, when the investigated system is close to the electron bottleneck regime and the dynamic terms that contain the susceptibilities of the localized angular momenta cannot be neglected. An exact solution of the coupled Bloch equations[11] for the magnetizations of the conduction electrons and the localized angular momenta was carried out with a computer. In the calculations we used the following quantities: conduction-electron g-factor $g_e = 2.26$, localized angular momentum g-factor $g_l = 1.99$, and exchange integral $J = 0.034$ eV as determined by us by experiment. As seen from Fig. 4, the theoretical curve describes adequately the experiment at $\delta_{eL} = 6\times10^9\ \mathrm{sec}^{-1}$.

The presence of superconductivity in samples with $H/Pd \geqslant 0.8$ makes it possible to compare the exchange integral J, determined from EPR measurements, with the data obtained from the dependence of the critical temperature T_c of the superconductor on the magnetic-impurity concentration, using the Abrikosov–Gor'kov equation

$$\Delta T_c = -\frac{\pi^2}{8k_B} J^2 N(E_F) cS(S+1), \tag{3}$$

where ΔT_c is the change of T_c as the result of introduction of the magnetic impurity, c is the concentration of the magnetic impurity. By measuring the critical temperature of samples with composition $H/Pd = 0.94$ and gadolinium concentrations 0.5 and 0.01 at. %, we obtained $\Delta T_c/\Delta c = 5$ K/at. %. This yields $J = 0.087$ eV. This value of the exchange integral is much larger than the corresponding value obtained from EPR measurements. The observed discrepancy may be connected with the fact that nonmagnetic scattering can also contribute to the decrease of T_c.

3. *Investigation of the effect of the conduction-electron mean free on the Ruderman–Kittel–Kasuya–Yoshida (RKKY) exchange interaction.* In samples with gadolinium concentration 0.5 at. %, a broadening of the EPR line corresponding to the α and β phases of Pd–H was observed at low temperatures. This behavior of the EPR line width can be due to effects of magnetic ordering on the localized states of the impurity,[12] which are connected by the RKKY indirect exchange interaction[13]

$$J_{\mathrm{RKKY}} = \frac{9\pi Z J_0^2}{2E_F}\,\frac{\cos 2k_F R}{R^3}, \tag{4}$$

where Z is the number of conduction electrons per atom, E_F is the Fermi energy, k_F is the Fermi wave vector, and R is the distance between the magnetic ions.

The magnetic-ordering temperature of the localized angular momenta is connected with the RKKY integral by the relation

$$k_B\Theta = \sum J_{\mathrm{RKKY}}, \tag{5}$$

where the summation is over the lattice. In real physical situations, the scattering of the conduction elec-

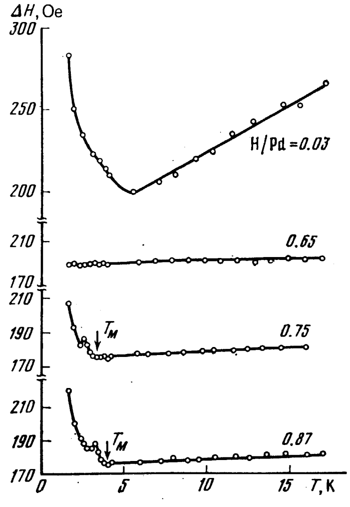

FIG. 5. Temperature dependence of the EPR line width of 0.5 at. % Gd in the α and β phases of the Pd–H system for several samples.

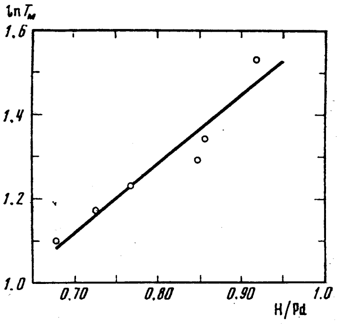

FIG. 6. Dependence of the temperature of the start of the EPR line broadening on the hydrogen concentration in the β phase of the Pd–Gd–H system with 0.5 at. % Gd.

trons by the impurities limits the conduction-electron mean free paths, and consequently weakens the RKKY interaction. A detailed theory of this phenomenon was developed by de Gennes.[14] He has shown that if the state density of the conduction electrons on the Fermi surface remains constant, then the RKKY volume exchange integral can be written in the form

$$J_{\mathrm{RKKY}}=\frac{9\pi ZJ_0^2}{2E_F}\frac{\cos 2k_F R}{R^3}\exp\left(-\frac{R_c}{\lambda}\right), \tag{6}$$

where λ is the conduction-electron mean free path and R_c is a certain characteristic distance.

The temperature dependence of the width of the EPR line in the α and β phases for some samples is shown in Fig. 5. As seen from the figure, in the β phase the temperature T_M, which corresponds to the start of the line broadening, depends on the hydrogen concentration in the sample. It can be assumed that this temperature is proportional to the magnetic-ordering temperature. The existence of the β phase in a wide range of hydrogen concentrations has made it possible to investigate the dependence of T_M on the hydrogen content in the sample. It turned out that this dependence is well described by an exponential function (see Fig. 6).

The dependence of T_M on the hydrogen content in the sample cannot be described by small changes of the state density of the conduction electrons in this region of hydrogen concentrations.[15] To explain the observed experimental fact we have performed measurements of the electric conductivity on the investigated samples (see Fig. 7). As seen from the figure, the conductivity increases in proportion to the hydrogen content in the sample. Since, as already indicated above, the state density of the conduction electrons in the β phase remains practically unchanged, it is natural to assume that the effective mass of the carriers is also current. It can be concluded in this connection that the changes of the conductivity observed by us are due to the linear dependence of the mean free path on the hydrogen content in the sample. Consequently, the dependence of the temperature of the magnetic ordering on the conduction-electron mean free path is described by an exponential function. Thus, a direct experimental confirmation has been obtained for the influence of the conduction-electron mean free path on the RKKY exchange interaction in accordance with the theoretical calculations carried out by de Gennes.

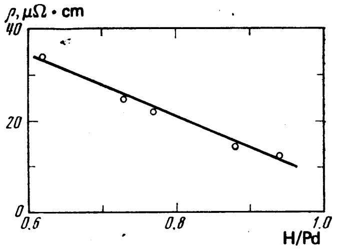

FIG. 7. Dependence of the resistance on the hydrogen concentration in the β phase of the Pd–Gd–H system containing 0.5 at. % Gd at 77 K.

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