CONDUCTION ELECTRON SPIN RESONANCE IN PALLADIUM

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Résumé.- L'observation récente de la résonance de spin des électrons de conduction du Palladium est décrite en détail. Cette observation qui est la première étude d'un métal de transition par cette méthode, permet de mesurer l'interaction électron-électron responsable de l'augmentation de la susceptibilité statique. Dans notre cas, cette interaction se traduit par l'apparition d'un signal de résonance étroit et intense et dont l'asymétrie est due à la présence d'ondes de spin paramagnétiques. Appliquant les méthodes classiques d'analyse des métaux simples au cas du Palladium nous en tirons le facteur g(Pd) = 2,25 ± 0,03, le coefficient d'augmentation de la susceptibilité $(m^*/m)\ (1+B_o)^{-1} \sim 16$ ainsi que la largeur de raie résiduelle à basse température inférieure à 100 gauss. De nombreux problèmes restent posés par la dynamique interne des électrons.

Abstract.- The recent observation of CESR in Palladium is described in detail. This is the first transition metal to be studied by this method, which allows also a determination of the electron-electron interaction responsible of the susceptibility enhancement. Indeed, this interaction gives rise to a resonance signal which is relatively narrow at low temperature (< 100 gauss residual width) and intense, and whose asymmetry is presently assigned to paramagnetic standing spin waves. Applying to the case of Palladium the classical analysis carried for simpler metals yields the g factor g(Pd) = 2.25 ± 0.03 and the susceptibility enhancement factor $(m^*/m)\ (1+B_o)^{-1} \sim 16$. However, a number of problems concerning the internal dynamics of electrons are left.

1. INTRODUCTION.- Palladium metal has been investigated in the last decade in an extensive manner for it's magnetic properties, band structure and transport coefficient. As we wish to contribute a new information concerning the spin resonance properties of this metal we will first recall some of the main features of Pd together with the classical results of spin resonance in simple metals.

Palladium being the last transition metal of the second serie should have a complete $4d^{10}$ shell. However due to s-d hybridization the Fermi sea contains 0.36 electron/atom and 0.36 hole/atom, as established by band structure /1/ and D.H.V.A. measurements /2/. The Fermi surface is divided into a Γ centered electron volume, roughly spherical, and a three dimensional d hole "jungle gym" of intersecting cylinders at point X in the classical notation of the fcc Brillouin zone polyhedron /1/. Remaining smaller volumes of electrons at X and recently discovered d holes at L will not concern us here as the density of state is overwhelmingly due to the d hole "jungle gym". Indeed this part is responsible for the large specific heat /3/, susceptibility /4/ and scattering properties /5/. As Pd is a moderately heavy metal spin orbit interaction has to be taken into account *a priori* in the band structure. As shown by a tight-binding calculation /6/ the effect of this perturbation is large only at selected points on the Fermi surface and this will play an essential role in the evaluation of g factors /1,7/. In contrast to spin orbit interaction, electron-electron and electron-phonon interactions are not included in the band structure calculation and their existence is mainly inferred from the difference between the calculated and measured quantities /2/. The electron-electron interaction leads to an enhancement of the spin susceptibility which has been described in the Landau Fermi liquid framework /8/ or in the equivalent paramagnon theory /9/. However this type of determination has yielded widely different values for these interactions so that a direct determination of it is important.

From the electron spin resonance point of view Palladium raises a number of experimental and theoretical problems as compared to the simpler metals studied by this technique so far (these are the alcalis and noble metals and Mg, Be and Al). The quantity which is measured is the transverse susceptibility of the conduction electron spins : in the case of a non-interacting electron gas Dyson /10/ and Feher and Kip /11/ have shown that the resonance occurs as a single peak at the Larmor precession frequency of the electrons, the analysis of which gives the g factor of the electrons, the spin life time T_2, the diffusion coefficient D of the electrons and a quantity proportional to the static Pauli sus-

ceptibility of the electrons. In presence of Fermi liquid interactions /12/ a detailed study of slabs of Na and K /13/ has revealed the presence of a serie of resonances in the immediate vicinity of the ordinary one : these have been shown to be paramagnetic spin waves whose dispersion relation directly gives access to the Fermi liquid parameters. In the case of the alcali metals, the spin enhancement is modest ($\sim$ 20 %) and the Fermi surface ideally simple, allowing a very detailed comparison with the theory. We will see that although much more pronounced, these effects are less suitably analysed in the case of Palladium.

Prior to our measurement a number of scattered information was available, pertaining to the probable spin resonance properties of Pd. Different estimate of g factors on the electron Fermi surface around X and Γ existed /1/,/6/ but only recently was made a calculation for the d hole "jungle gym" /7/, giving g(d holes) = 2.31, on average, with very large anisotropy from $g < 0.5$ to $g > 3$. Experimentally, spin splitting zeroes from DHVA work /2/ reveal also g values at selected points but do not correspond to the quantity measured in a dynamical experiment. A particular determination of g is available through the magneto-mechanical factor g' measured by Huguenin and coworkers /14/ finding g'(Pd) = 1.77 at room temperature, from which it follows from the relation $g - 2 = 2 - g'$ that g(g') = 2.23. The most encouraging prediction came, in fact, from the study of spin resonance of dilute alloys of Mn in Pd by Alquie and coworkers /15/. They showed that, as the Mn spin was strongly coupled to the Pd electron spin, they could, by extrapolating their results to vanishing Mn concentration, predict the dynamical properties of Pd to be : g(Pd) = 2.25 ± 0.01 at Helium temperature and, most important, a linewidth of 250 gauss and a signal intensity in agreement with the static susceptibility. This prompted us for a direct search on pure Palladium metal.

2. EXPERIMENTAL TECHNIQUE AND RESULTS.- The technique we have been using is that of spin transmission /13/. This technique is ideally suited for the study of pure metals where the mean free path is long and the conduction electron spin signal intensity low and easily confused with the background. The case of Pd appears to be marginal in that the resonance signal intensity is very large and that the spin diffusion coefficient seems very much smaller than that of monovalent metals. Indeed pure Pd resonance has been observed as well with the more common reflection technique /16/. The transmission technique is however essential for the study of the excitation and propagation of paramagnetic spin waves. We simply recall that the sample is in the form of a thin foil clamped tightly between two symmetric TE 101 cavities tuned at 9.2 GHz. The exciting cavity is fed by the r.f. generator and induces spin resonance on one face of the sample. Those electrons which will diffuse across the sample thickness in a time shorter than their transverse relaxation time T_2 emit a coherent radiation in the other cavity, which is detected by it's projection on a suitable reference phase, by a balanced mixer. In the case of a very thin and pure metal slab standing spin waves occur : if a dispersion relation exists, $\omega(k)$, this will give rise to a separate resonance for each k value selected by the boundary conditions /8/. The requirement for sample preparation are : 1) high purity, high resistance ratio ; 2) very thin. We have purified commercially available Pd by prolonged oxydation in air at 1200°C in a quartz tube. Three consecutive steps of rolling and annealing were then necessary to achieve a final thickness of 5 to 15 microns. The final, highly polycristalline foils, had a resistivity ratio which was size dependent at a rate of $\Delta\rho_{(size)} = 5 \pm 1 \times 10^{-3}$ $\nu\Omega cm.cm^{-1}$, indicating surface scattering, and extrapolating to a bulk resistivity ratio $\geq$ 2.000. Great care was taken to avoid hydrogen contamination. The thickness was estimated (to about 3 %) by weighting and surface measurement.

Although great care was used to mount the samples tightly between the resonating cavities very large r.f. power was transmitted at room temperature by the thinnest samples. This was easily traced back to be due to the direct skin effect transmission as it strongly decreases upon cooling, together with a rotation of the phase of 132° per decade amplitude change (as expected from the transmission coefficient $\exp -(1 + i)\ell/\delta(T)$). It disappeared below nitrogen temperature.

At temperatures below 20 K large spin resonance were visible as shown in figure 1 and 2, superimposed on a very uniform background of orbital transmission (unresolved cyclotron motion). However as compared with a normal metal conduction electron resonance the Pd signal has many uncommon features that we have to describe in detail.

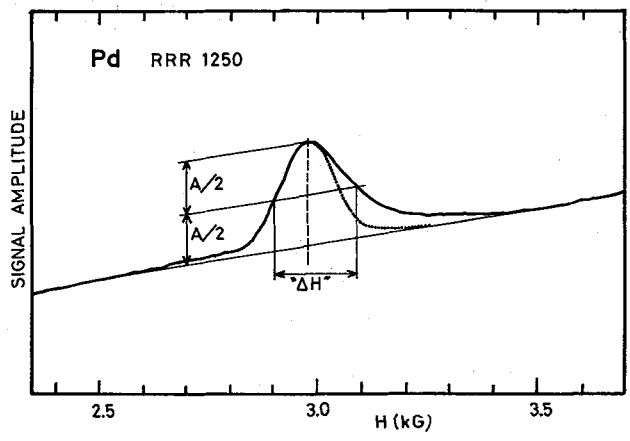

Fig. 1 : Typical trace recording of Pd spin resonance. The sample thickness is 15 μm and the temperature 4.0 K. The asymmetry in the line shape is made apparent by the dotted line which has been drawn to be symmetric to the low field side of the line with respect to the maximum point. This signal is isotropic with the magnetic field direction with respect to the sample and corresponds to a situation where the thickness is about equal to the spin mean free path. The reference phase used is shifted by 110° from that of normal metal spin resonance

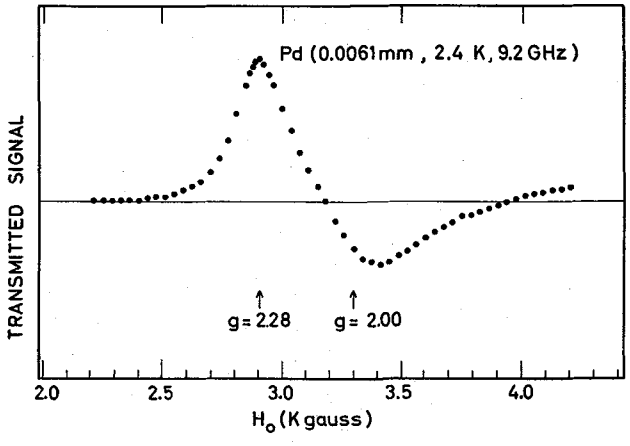

Fig. 2 : Pd spin resonance for a thin sample where the thickness is less than the spin mean free path. The reference phase is set at the "normal" metal phase. The high field negative lobe is isotropic and is interpreted as a manifestation of a standing spin wave. A substraction of a sloping base line has been operated

It appears at first sight that in figures 1 and 2 the resonance signal cannot be made to appear like a symmetric Lorentzian line. Such a situation can occur in the alcali metals /13/ or in aluminium /17/ and is a manifestation of unresolved spin waves. We have tried to get rid of the asymmetry of the shape in different ways 1) by increasing the temperature, the scattering rate is increased and indeed the asymmetry is decreased but so is the intensity of the signal which vanishes (see fig.3) above 22 K without developing the characteristic shape /18/ (with A and B lobes) typical of transmission of a normal metal of thickness larger than the spin mean free path /19/. 2) By changing the magnetic field angle with respect to the sample the signal shape and amplitude is observed to be completely isotropic, to better than a few %, in complete contradiction with usual spin waves spectra. 3) By changing the sample thickness the shape of the asymmetry is modified from figure 1 to figure 2 and also the reference phase used. For our thinnest Pd sample the reference phase is that used for a normal metal /18/. In as much as one can define a g factor by the position of the peak of the least asymmetric signal, this parameter is observed to change slightly with sample thickness and on the average of six samples is g(Pd) = 2.25 ± 0.03. From figure 4 it appears to be independent of temperature at low temperature. The linewidth is also tentatively defined as the width at half height. Figure 5 shows how it increases with increasing temperature /20/. The residual width (extrapolated at 0 K) contains a contribution which is size dependent at a rate of 0.1 gauss/cm^{-1} indicating an unusually large surface spin scattering term.

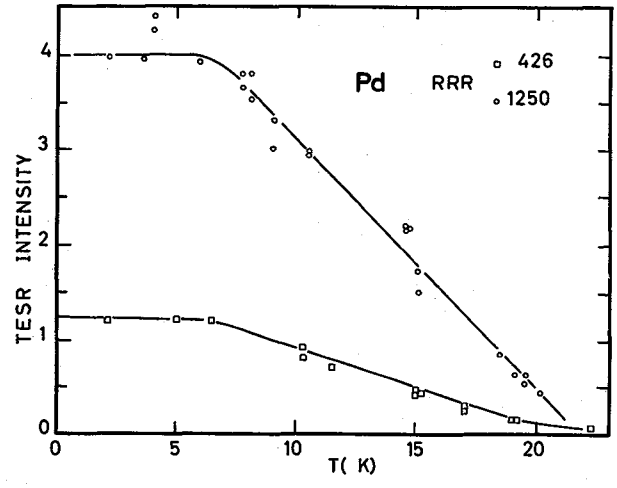

Fig. 3 : The intensity of the resonance for the signal of figure 1 *versus* temperature (0). The squares (□) refer to the same sample after spoiling the resistivity ratio. Although definitely in the "thick limit" case where the thickness is larger than the spin mean free path, the observed signal shape fails to develop A/B lobes as the temperature increases. See references /17/ and /18/

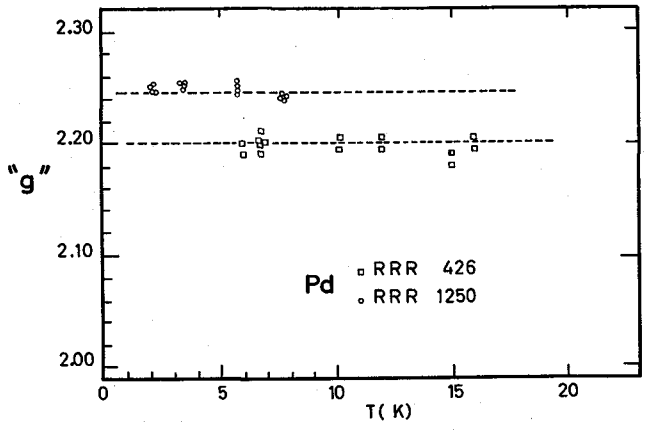

Fig. 4 : "g" factor as a function of temperature defined by the position of the resonance peak for the least asymmetric signal phase setting. The large variation observed between two samples is an illustration of the lineshape problem

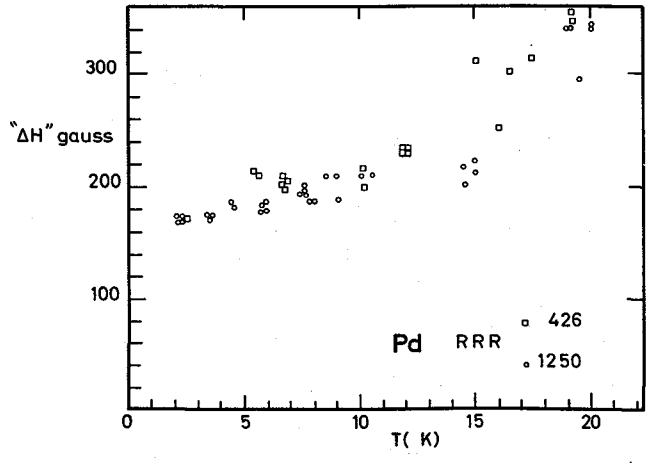

Fig. 5 : The line width at midheight of the (asymmetric) signal as a function of temperature. The data above 10 K should not be used without proper correction for lineshape. For comparison see reference /15/

3. ANALYSIS AND DISCUSSION.- In the case of a normal metal of thickness less than the spin mean free path the transmitted signal is given by /19/ :

$$h_t = i\,\pi\,h_o\,\frac{\delta^2}{\lambda \ell}\,\frac{\chi\,\omega}{(i(\omega - \omega_o) + \frac{1}{T_2})} \qquad (1)$$

where h_o is the exciting field, δ the normal skin depth, λ the free space wavelength of the radiation at frequency ω, ℓ the sample thickness, χ the Pauli susceptibility of the metal and $\omega_o = \frac{g\mu_B}{\hbar} H_o$ is the Larmor frequency of the spins. We will discuss these different parameters in turn :

Most important is the signal intensity defined by the product of the signal height by the line width : this quantity is proportionnal to (χ/ℓ) and is found to be constant for $\ell < 9$ microns. We have compared this quantity to the same one determined with copper samples /21/. This allows to determine approximatively the ratio of the spin susceptibilities/cm^3 of two metals as we use the same geometrical conditions. We find

$$\left(\frac{\chi/\mathrm{cm}^3\ (\mathrm{Pd})}{\chi/\mathrm{cm}^3\ (\mathrm{Cu})}\right) = 33 \pm 10 \ \text{(spin resonance)}$$

where the large uncertainty reflects the undeterminacy of the anomalous skin depth in each case. By comparison it should be noted that the ratio of the measured static susceptibility of Pd at He temperature to the (calculated) Pauli susceptibility of copper gives

$$\frac{\chi/\mathrm{cm}^3\ (\mathrm{Pd})}{\chi/\mathrm{cm}^3\ (\mathrm{Cu})} = 87 \ \text{(static)}$$

so that the large intensity inferred by resonance is only a fraction of the total susceptibility measured ; nevertheless this crude comparison establishes the fact we are indeed observing the d hole spin resonance of Palladium. This is in accordance with the ratio of susceptibilities of Mn impurities and Pd electrons inferred by Alquie /15/. Although the linewidth, and correspondingly T_2, are poorly defined experimentally it is possible to define a low temperature region below 10 K where the width is approximately constant : as this residual linewidth contains an important contribution from surface scattering, one determines the bulk linewidth by extrapolating our data to zero inverse thickness. This gives

ΔH(bulk, residual) = 75 ± 25 gauss and

$T_2 = (\gamma \frac{\Delta H}{2})^{-1}$ of the order of 2×10^{-9}s. From the measured spin surface scattering rate, one can estimate the spin flip probability ε per collision at the surface. In the notation of Dyson /10/ this is twice the ratio of the spin transit time ℓ/v_F by the surface spin flip time, we find :

ε(Pd surface) = 1×10^{-2}

if we take $v_F = 5 \times 10^7$ cm/s. A similar estimate of ε can be made using the measured resistivity increment due to size effect.

Subject to modification from a computer fit lineshape analysis (which we have not carried out in view of the large number of ill defined parame-

ters) the g valued has been defined, as mentioned at the peak of the resonance signal. In view of the very large g value distribution /7/ it is tempting to attribute some, if not all, of the asymmetry in the signal shape to an incomplete narrowing of this distribution. However a rapid estimate shows that the narrowing factor must be of the order of 100 at least, ensuring a Lorentzian lineshape. In order to study this dynamical process the frequency dependence of the residual linewidth should be investigated /22/. The physical origin of this strong narrowing that allows our observation of a unique, well defined resonance, is probably due to the strong electron-electron interaction exchange as explained by Freedman and Fredkin /23/.

We have tentatively attributed the negative high field lobe visible on the spin resonance signal of figure 2 to a barely resolved standing spin wave for the following reasons : the classical derivation of spin wave /12/ gives very anisotropic spectra only because the cyclotron motion determines an anisotropic diffusion constant in the limit $\omega_c \tau > 1$, where $\omega_c = \frac{eH}{m^* c}$ is the cyclotron frequency. In our case however a rough estimate shows that $\omega_c \tau \simeq 0.1$. This is more than enough to kill any spin wave propagation in the usual metals where the electron-electron interaction is moderate since the criterion for spin wave resolution is /12/ :

$$X = \left| \frac{-B_o}{1 + B_o} \omega_o \tau \right| \geq 1 \qquad (2)$$

where $\frac{1}{1 + B_o}$ is the susceptibility enhancement expressed in the Fermi liquid notation /8/, assuming higher order coefficients to be zero. We hint from the fact that $\omega_o \tau > \omega_c \tau$ and that the enhancement is sizeable, that this criterion is still approximately satisfied in our case. The shift of the spin waves then becomes <u>isotropic</u> and is given by the field perpendicular classical case which we write for the n = 1 spin wave /8/ :

$$\Delta\omega(n = 1) = - \frac{\pi^2}{3} \frac{\hbar^2}{m^2} \frac{k_F^2}{\ell^2 \omega} \frac{(1 + B_o)^2}{(\frac{m^*}{m})^2} \frac{1}{B_o} \qquad (3)$$

where m is the bare electron mass and $\hbar k_F = m^* v_F$ the Fermi momentum. We have checked on samples of 6.1, 7.0 and 8.9 microns that this negative lobe was shifted, in accordance to (3), as the square of the inverse thickness towards high fields /24/. However no n = 2 resonance could be detected, mainly because of severe base line substraction problems.

In order to use (3) we assume that k_F is determined by the volume of the Fermi sea containing 0.36 el/at, thus avoiding Fermi velocity determination. We take $kF = 0.897 \times 10^8 cm^{-1}$. We find from (3) /24/ that :

$$(\frac{m^*}{m})^2 \frac{B_o}{(1 + B_o)^2} = - 195 \pm 20 \qquad (4)$$

and, assuming that $\frac{m^*}{m} = 3.3$ (for sake of estimate) we get :

$B_o = - 0.8$

and,

$$(\frac{m^*}{m}) \frac{1}{1 + B_o} = 16 \qquad (5)$$

in poor agreement with estimates from the static susceptibility. This last parameter (5) is seen to be quite independent of the choice of m^*/m if $B_o \sim - 1$. We check that the condition (2) is fullfilled for $\omega_o \tau > 0.25$. We note that an equivalent manner to analyse our data is to evaluate the diffusion coefficient using the conductivity /25/, /26/, /27/. We see that any improvement in this type of determination rests on our experimental effort to observe better defined spinwaves but also a better understanding of the internal dynamics of s and d electrons allowing a knowledge of the diffusion parameters to be used for spinwave propagation.

We have not dealt, in this experimental presentation, with many aspects of the spin resonance of Palladium which merit further investigation, either for their intrinsic interest for the resonance itself such as the problem of lineshape in reflection /16/ or for the physics of Palladium, such as the connection between the temperature dependent linewidth /15/ and the AT^2 term in the resistivity, characteristic of s-d scattering /5/. As a conclusion of this ensemble of observations, the main fact remains the very unexpected "goodwill" of the Pd electron spins to display a rather narrow resonance. In our interpretation it's, somewhat unusual, characteristics are due to electron-electron interactions and hopefully this will provide a way to understand better the physics of transition metals.

ACKNOWLEDGMENTS.- Acknowledgments are gratefully extended to H. Hurdequint for this numerous suggestions and collaboration and to G. Alquie thanks to whom this work was started. We thank Mrs. Marguerite Boix for her pertinent help in purifying the samples. M.T. Beal-Monod is indebted for illuminating private communications.

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/26/ The same problem arises in reference /18/ for the case of Li and the same line of argument is used. Note that there exists only one type of electrons in that case

/27/ It should be stressed that the almost resolved spectra observed is in itself quite remarquable, in view of the spread of $\frac{m^*}{m}$. It is conceivable that the physical variable would be the combination appearing in equation (5). We note in that derivation $\frac{m^*}{m}$ does not contain electron-phonon interaction and thus should be compared with specific heat results : c.f. Herring, Magnetism, (Academic Press) 1966, vol. IV, p. 290.