Absence of magnetic field dependence of the cyclotron effective masses of electrons on the Fermi surface of Pd

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The de Haas—van Alphen effect was used to search for a field-dependent many-body enhancement of the cyclotron effective mass in palladium, an effect suggested by experiments observing a depression of the electronic specific heat by a magnetic field. Sixteen orbits on the open hole, Γ-centered electron, and X-centered hole sheet of the Fermi surface of Pd were studied with the field-modulation technique in fields up to 15 T and at temperatures as low as 0.5 K. For the heavy-mass β and γ orbits on the open hole sheet we find effective masses approximately 15% higher than reported earlier, while results for the other orbits confirm earlier work. Within experimental error no field dependence in the cyclotron effective mass was found for any orbit, implying that a large reduction in the linear term of the specific heat by a magnetic field is not due to a suppression of spin fluctuations. In addition, the field dependence in the argument of the spin-splitting factor in the Lifshitz-Kosevich expression for the amplitude of the de Haas—van Alphen effect was measured for the α orbit on the open hole sheet. The small field dependence observed is inconsistent with a large suppression of spin fluctuations, but is consistent with high-field magnetization measurements.

I. INTRODUCTION

The observation of a magnetic field-dependent electronic specific heat in several strongly exchange-enhanced paramagnetic metallic compounds (for $LuCo_2$, YCo_2, and $ScCo_2$, see Ikeda and Gschneidner[1] and Ikeda *et al.*;[2] for $CeSn_3$, see Ikeda and Gschneidner[3] and Tsang *et al.*;[4] for $TiBe_2$, see Stewart *et al.*;[5] for UAl_2, see Trainor *et al.*[6] and Stewart *et al.*[7]) and elements (for Sc, see Ikeda *et al.*;[8] for Pd, see Hsiang *et al.*;[9] and for *Pd*Ni, see Ikeda *et al.*[10]) suggests the possibility that spin fluctuations are important in transition, rare-earth, and actinide metals. The reduction of the spin-fluctuation contribution to the electronic specific heat at high magnetic fields is well established theoretically (Doniach and Engelsberg,[11] Berk and Schrieffer,[12] de Chatel and Wohlfarth,[13] Schrieffer,[14] Béal-Monod *et al.*,[15] Brinkman and Engelsberg,[16] Hertel *et al.*,[17] Béal-Monod,[18] Béal-Monod and Daniel,[19] and Béal-Monod and Lawrence,[20]) although the magnitude of the depression predicted by theory is generally smaller than that which is observed.

Among the elements, Pd is traditionally taken as the best candidate for observing spin fluctuations because of its high electronic density of states and large Stoner enhancement in the magnetic susceptibility. Specific-heat experiments by Hsiang *et al.*[9] showed a reduction in the electronic specific-heat coefficient γ_{el} of 7% in a magnetic field of 10 T, suggesting that strong spin fluctuations occur in Pd. This interpretation was supported by earlier de Haas—van Alphen (dHvA) measurements by Dye *et al.*[21] of the cyclotron effective masses in high fields, which implied an electronic density of states at the Fermi level derived from a Korringa-Kohn-Rostoker (KKR) parametrization which was $\sim 15\%$ below that measured at zero fields in specific-heat experiments. In order to prove the presence of spin fluctuations, it is necessary to show that any field-dependent signature occurs in the itinerant electrons and is not due to a local effect such as magnetic impurities. The most suitable experiment for this purpose is the observation of a depressed cyclotron effective mass as a function of magnetic field using the dHvA effect, because these measurements probe only the itinerant electrons and are insensitive to local effects. Furthermore, Pd is especially well suited for such experiments because good crystals are available and its Fermi surface properties are well established.

In this paper we report the detailed results of a search for a field-dependent cyclotron mass in Pd. A brief summary of our results was given earlier (Joss *et al.*[22]). We have examined several orbits on the open hole, Γ-centered electron, and X-centered hole sheets of the Fermi surface, finding no field dependence in the mass within experimental error. Furthermore, more extensive measurements of the masses on the open hole sheet in higher fields and with more sensitivity than were previously available lead to a KKR-parametrized density of states which differs from the zero-field specific-heat value by no more than $\sim 2.5\%$ rather than $\sim 15\%$ as estimated earlier. Measurements of the argument of the spin-splitting factor in the Lifshitz-Kosevich (LK) expression at the spin-splitting zero of the α orbit on the open hole sheet reveal only a tiny field dependence, inconsistent with a large suppression of the spin-fluctuation contribution to the magnetic susceptibility. Our results imply that a large reduction in the linear term of the specific heat by a magnetic field is not a property of the conduction-electron system and therefore is not due to a suppression of spin fluctuations. These conclusions are supported by more recent specific-heat experiments on different samples by Franse[23] to 5 T and by Stewart and Brandt[24] to 20 T which show no change in γ_{el} with field.

In the following paper (Joss and Crabtree[25]), the results of a KKR parametrization of the effective mass data are presented together with a discussion of the variation of the many-body enhancement of the mass over the Fermi surface.

II. EXPERIMENTAL TECHNIQUE

The Fermi surface (FS) of Pd consists of four sheets.[21] Three of these contain holes (the X-centered fourth-band pockets, the L-centered fifth-band pockets, and the fifth-band open hole sheet) and one contains electrons (the Γ-centered sixth-band sheet). Because Pd is a compensated metal the total volume of the hole sheets is equal to the volume of the electron sheet. However, the total volume of the L- and X-centered hole pockets is less than 2% of that of the open hole sheet,[21] so that to a good approximation the carriers may be assumed to be divided equally between the Γ-centered electron sheet and the open hole sheet. The contribution of each of these sheets to the enhanced electronic density of states at the Fermi level is estimated in the following paper:[25] 87% from the open hole sheet, 9% from the Γ-centered electron sheet, and 4% from the L- and X-centered sheets. Because the open hole sheet dominates the density of states, it is important to look for a field dependence in the masses associated with this sheet. The topology of this sheet and the orbits it supports are shown in Fig. 1. If a 7% depression in the density of states is to be accounted for by the Γ-, X-, and L-centered sheets only, their density of states must be reduced by a factor of ~ 2 which is greater than the total many-body enhancement due to electron-phonon and electron-electron interactions combined.[25] For this reason we concentrated our mass measurements on the open hole sheet. However, it is possible that the Γ- and X-centered sheets show a field dependence which is easier to measure because the dHvA signals are stronger. Therefore, we examined a few representative orbits on these sheets as well.

A. Sample preparation and measurement technique

The sample used in the present experiment is the same as was used by Dye *et al.* It was prepared by repeated float zone refining in air (Sandesara and Vuillemin[26]) of high-purity Pd. The final residual resistivity ratio as measured with a four-wire dc technique and extrapolated to $T=0$ was in excess of 25 000.

Measurements of the dHvA effect were made using low-frequency large-amplitude field modulation in fields as large as 15 T and at temperatures as low as 0.5 K. The second harmonic of the modulation frequency was used for detecting the oscillations. The signals were digitized to allow on-line Fourier analysis of the oscillations into frequency-dependent amplitude and phase. Effective masses were derived from the temperature dependence of the dHvA amplitude with temperatures determined by vapor-pressure thermometry. Vapor pressures were measured using two different methods: utilization of capacitance manometer (Datametrics Barocell) and quartz Bourdon tube (Texas Instruments differential pressure gauge).

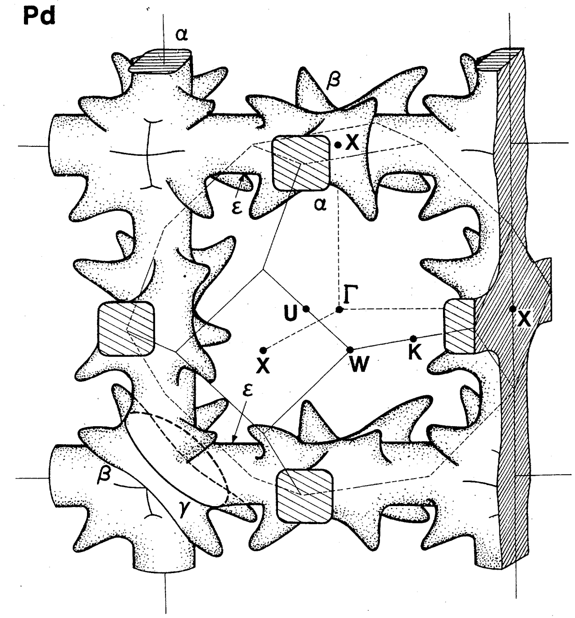

FIG. 1. Fifth-band open hole sheet (scaffolding) of the Fermi surface of Pd [after A. R. Mackintosh and O. K. Anderson, in *Electrons at the Fermi Surface,* edited by M. Springford (Cambridge University Press, Cambridge, 1980), p. 207] showing representative extremal orbits ($\alpha,\beta,\gamma,\epsilon$), the Brillouin zone, and high-symmetry points. The protruding "fins" centered at the X point contribute strongly to the density of states.

B. Mass measurements

1. *Orbit choice*

The low frequency of the orbits on the L-centered pocket prevents high-field measurements of the masses because the modulation amplitude required to optimize the signal is larger than our system can provide, and because the number of oscillations occurring in a typical high-field data window is too small for an accurate Fourier analysis. In addition, the masses on this sheet are high enough to make accurate low-field measurements difficult because the signals are weak. Therefore, no mass data were taken on the L-centered pocket.

The smaller masses of orbits on the X-centered pocket allowed mass measurements to be made on the dHvA harmonics of the signal. This eliminated the problems arising from the low frequency of the fundamental and provided a greater change of amplitude with temperature at high field allowing a greater accuracy in the mass measurements.

On the Γ-centered electron sheet there is little anisotropy in the Fermi surface properties and therefore no need to examine many orbits for field-dependent masses. We chose the [011] orbit as representative of this sheet because it passes all three high-symmetry directions, where there are variations in the Fermi velocity (see following paper). The signals on the Γ-centered sheet are the strongest in Pd and provide the most accurate mass data.

Most of the data were taken on the open hole sheet. Masses on this sheet are the most difficult to measure because the signals are weak due to the high masses and because the dHvA frequencies of interest are embedded in a series of closely spaced higher harmonics of the X pockets as illustrated in Fig. 2. Avoiding this interference between frequencies requires a careful choice of the field direction appropriate for each open hole orbit. In order to discriminate against the very strong signals from the Γ-centered electron sheet the modulation amplitude was set so that the Bessel function for this orbit was on a zero, and the Bessel function of the open hole orbit of interest was near the first maximum. In spite of this precaution, a small fraction of the signal from the Γ-centered sheet invariably leaked through. To obtain sufficient resolution of the open hole signals from the X-centered harmonics, a large number of oscillations in the data window was required, causing aliasing of the Γ-centered frequencies. A Fourier spectrum for the field 76° from [100] in the $(01\bar{1})$ plane is shown in Fig. 3. There it can be seen that for this field direction the 12th and 13th harmonics of the degenerate X pockets centered at (0,1,0) and (0,0,1) interfere slightly with the open hole γ and β frequencies. The sampling rate and data window were chosen to alias the second harmonic of the Γ-centered electron sheet into a region of the spectrum far from the open hole frequencies.

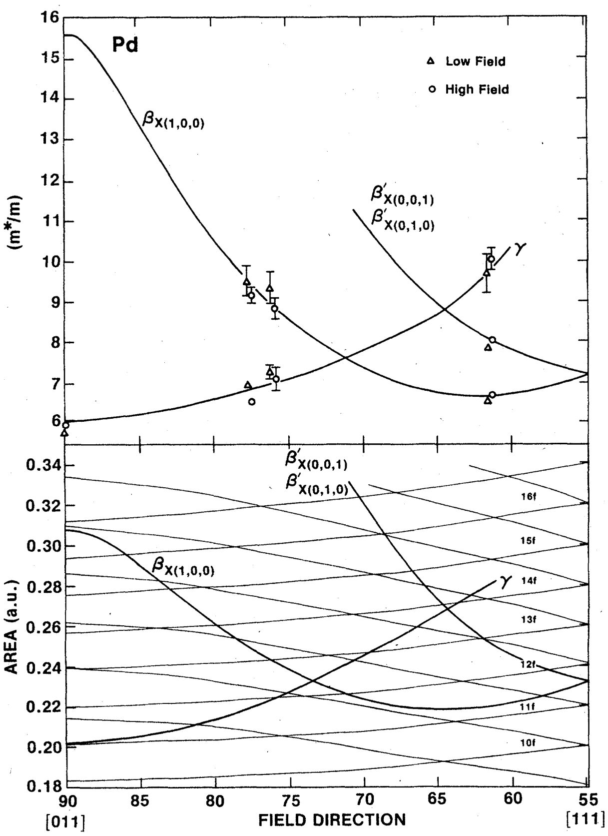

FIG. 2. Angular variation of the cyclotron effective masses (upper part) and cross-sectional areas (lower part) for the β, β', and γ orbits in the $(01\bar{1})$ plane. The symbols in the upper part are measurements at low fields of ~ 11 T and high fields of ~ 13 T (exact values given in Table I), and the solid lines are the results of a KKR fit to 27 masses on the Pd Fermi surface (see Joss and Crabtree, following paper, for details of the KKR fit). The heavy lines in the lower part of this figure are the KKR fit to the cross-sectional areas of the β, β', and γ orbits, and the light lines are the harmonics of the X-centered pockets.

2. *Error analysis*

Each mass was derived from amplitude measurements at temperatures spaced 0.05 K apart starting at 0.5 K. The stronger signals could be seen as high as 1.2 K, giving as many as 15 different temperatures, while for the weaker signals fewer temperatures were used. The errors were derived from three different sources: statistical uncertainty in fitting the measured amplitude A versus temperature T to the LK form, uncertainty in the field H, and errors caused by interference from nearby frequencies. Masses m^* were calculated by an iterative procedure which properly accounts for the sinh term in the LK formula. The first iteration fit $\ln(A/T)$ to T using a linear-regression algorithm. The slope $a=\alpha m^*/H$ of this fit gave the first estimate of the mass, which was then used in the second iteration where $\ln(A[1-\exp(-2\alpha m^*T/H)]/T)$ was fitted to T by linear regression, where $\alpha=14.69$ T/K. This process was continued until the slope of the line changed by less than some test amount. To account for the greater precision of the amplitude measurements at low temperatures, each amplitude was weighted by the quantity $A[\ln(A/T)-\exp(-2\alpha m^*T/H)]$. The linear-regression algorithm gives a statistical error in the slope of the line which can be converted to a statistical uncertainty in the mass.

In cases where interference from a nearby frequency could not be completely eliminated by adjusting the field

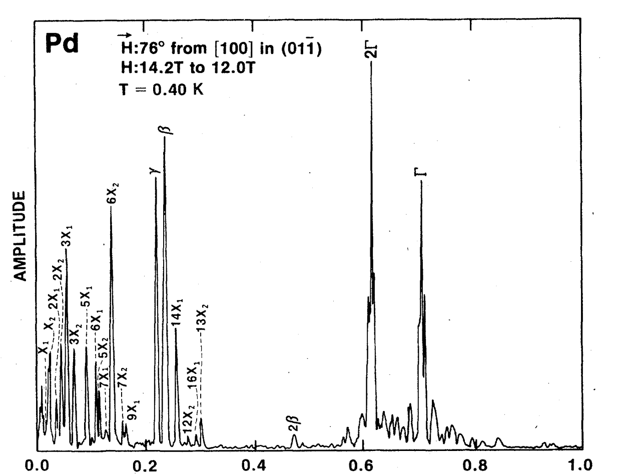

FIG. 3. Fourier spectrum of the frequencies in Pd for the field 76° from [100] in the $(01\bar{1})$ plane, showing the open hole γ and β frequencies and the interfering harmonics from the X-centered hole pockets. The second harmonic of the Γ-centered sheet (2Γ) has been aliased.

direction, an estimate was made of the uncertainty in the mass caused by the interference effects. Examination of the Fourier spectrum gives the amplitude ΔA of the tail of the neighboring frequency at the frequency of interest. Because amplitudes add coherently in the spectrum, the amplitude of the neighboring frequency can either add or subtract from the frequency of interest, raising or lowering the mass. The effect of these interfering amplitudes on the mass was estimated by finding the change in slope of the linear regression caused by adding or subtracting the amplitude ΔA of the neighboring frequency at high and low temperatures. This leads to the expression

$$\Delta a = \frac{\Delta A_1/A_1 - \Delta A_2/A_2}{T_1 - T_2} ,$$

where Δa is the change in slope of the linear regression and the subscripts 1 and 2 refer to high- and low-temperature points.

The final source of error is uncertainty in the field which was taken to be 1% in all cases. The total error in the measured mass was then computed by taking the square root of the sum of the squares of the three contributions.

C. Spin-splitting measurements

A second method for observing the field dependence of spin fluctuations is based on spin-splitting effects in the dHvA effect. Formally these effects are described by the spin-splitting factor $\cos(\pi g m_b/2m)$ in the Lifshitz-Kosevich expression for the amplitude of the oscillations. This factor arises from the interference between the oscillations for the spin-up and spin-down Fermi surfaces, which have slightly different cross-sectional areas due to the Zeeman splitting of the Landau levels by the external field. The phase difference between the spin-up and spin-down signals is proportional to the difference in the areas of the associated orbits

$$\Delta A_0 = \left[\frac{\partial A_0}{\partial E} \right] g\mu_B H .$$

The factor $g\mu_B H$ is the Zeeman splitting in energy for the orbit and the derivative is related to the effective mass m_b according to

$$\frac{m_b}{m} = \frac{\hbar^2}{2\pi} \frac{\partial A_0}{\partial E} .$$

The interference between spin-up and spin-down signals leads to a reduction in the amplitude described by the spin-splitting factor. The argument of the cosine factor given above is correct for the usual case where spin-fluctuation effects can be ignored.

It is important to note that the mass m_b occurring in the spin-splitting factor is the bare band mass, unrenormalized by electron-phonon or other many-body interactions. Intuitively this is clear from the preceding discussion because the phase difference arises from the difference between the spin-up and spin-down cross-sectional *areas*, a geometrical property of the Fermi surface which is not affected by many-body interactions. Although rigorous derivations of this result have been given by Engelsberg and Simpson,[27] Engelsberg,[28] and Riseborough,[29] it does not seem to be generally appreciated by experimentalists.

If spin fluctuations are important there is a field-dependent contribution to the electron self-energy which is absent in the case of electron-phonon interactions. If only the linear term in the field dependence of the self-energy is retained, the field-dependent part of the self-energy has the same form as the Zeeman splitting of the bare energy. This formal similarity allows the field dependence of the bare energy and self-energy to be combined and treated as a renormalized Zeeman splitting, leading to a phase difference between the spin-up and spin-down signals which is enhanced by the spin fluctuations. Rigorous derivations[27–29] show that the signal reduction due to spin splitting is given by $\cos(\pi S g m_b/2m)$, where S is the Stoner factor describing the enhancement of the magnetic susceptibility. It is important to note that in this approximation the spin-splitting factor does not reflect a field dependence in the mass because only the bare band mass appears in the argument of the cosine factor. The appearance of S in the argument of the spin-splitting factor reflects the enhancement of the bare g factor by spin fluctuations and is unrelated to any enhancement of the mass.

The difference in cross-sectional areas between the spin-up and spin-down Fermi surfaces which leads to the spin-splitting factor can be integrated over the Fermi surface to give the difference in volume between the spin-up and spin-down surfaces. This connection suggests that the argument of the spin-splitting factor is proportional to the orbital contribution to the spin magnetization; that is,

$$M = \mu_B^2 H \frac{m}{h^2} \int g(k_z) \frac{m_b(k_z)}{m} S(k_z) dk_z , \qquad (1)$$

where $\vec{k}_z = \vec{k} \cdot \hat{H}$ and the integral ranges over all possible cyclotron orbits for a given field direction. In the limiting case of no spin fluctuations ($S=1$) and $g(k_z)$ constant, the above reduces properly to the Pauli spin magnetization which contains the bare band density of states coming from the integral of the band mass m_b over the Fermi surface. If spin fluctuations are present, Eq. (1) correctly gives the low-field susceptibility $S\chi_{\text{Pauli}}$.

There is no field dependence in either the spin-splitting factor $\cos(\pi S g m_b/2m)$ or the susceptibility M/H given by Eq. (1) because in the derivation leading to these expressions the self-energy was expanded only through terms linear in the field. To derive the field dependence of the spin-splitting factor higher-order terms need to be included. No such calculation has yet been carried out. However, the field dependence of the spin-splitting factor can be inferred from that for the full magnetization. One such calculation, by Béal-Monod and Daniel[19], finds, at $T=0$ for a parabolic band

$$M/H = S\chi_{\text{Pauli}} \left[1 - \frac{1}{6} S^3 \frac{H^2}{T_F^2} + \cdots \right] .$$

According to this calculation, the field dependence of the argument of the spin-splitting factor should be given by

$$\frac{\pi S g}{2} \frac{m_b}{m} \left[1 - \frac{1}{6} S^3 \frac{H^2}{T_F^2} + \cdots \right] ,$$

where S in the above expression is the Stoner factor for a single orbit rather than for the entire Fermi surface.

From this discussion it can be seen that the argument of the spin-splitting factor depends on spin fluctuations in a different way than does the effective mass. The argument of the spin-splitting factor gives the orbital contribution to the magnetization (divided by field) while the effective mass gives the orbital contribution to the electronic specific heat. The spin-fluctuation enhancement in both quantities is reduced by a large magnetic field, but not necessarily by comparable amounts. The relation $\gamma_{el} \sim \ln \chi$, valid for parabolic bands and large Stoner enhancement as shown by Schrieffer,[14] suggests that measurable effects appear in the argument of the spin-splitting factor before they appear in the effective mass. However, the influence of the detailed band structure on the spin-fluctuation contribution to the susceptibility and electronic specific heat can be enormous as shown by MacDonald[30] and by Béal-Monod and Lawrence.[20] Following Engelsberg[28] we note that as Ni is added to Pd both γ_{el} and χ increase in the ratio $(\Delta\gamma_{el}/\gamma_{el})/(\Delta\chi/\chi) \sim 0.2$ (Schindler and Mackliet,[31] and Chouteau *et al.*[31]). This experimental result indicates that in Pd the argument of the spin-splitting factor is about five times more sensitive to spin-fluctuation effects than is the effective mass.

III. RESULTS

A. Masses

1. Comparison with earlier work

The results of the mass measurements are shown in Table I. For the $X(1,0,0)$-centered hole pocket the masses at [100] are within 3% of the values found by Windmiller *et al.*[32] and Roeland *et al.*[33] The masses on the same pocket at [010] agree within 3% with those measured by Windmiller *et al.* (Refs. 32 and 34), Venema,[35] and Ernest *et al.*[36] which range from 1.03 to 1.06. On the Γ-centered electron sheet the mass at [011] differs by less than 3% from that of Windmiller *et al.* Our central and noncentral masses at 61.4° are slightly smaller than those measured at [111] by Windmiller *et al.*, but the agreement is satisfactory considering the experimental error and difference in angle.

The errors for the masses on the open hole sheet are larger than those for masses on the other sheets due to weak signals and interference from the X pockets as described above. The α orbit at [100] occurs at nearly the same frequency as the third harmonic of the pockets centered at $X(0,1,0)$ and $X(0,0,1)$ leading to a large uncertainty in its mass. Because the mass of the X harmonic is larger than that of the α orbit, this interference effect is more serious at low field than at high field as reflected in the error bars in Table I. The low-field value shown there is consistent with the measurement of Windmiller *et al.*, which was made at comparable fields without Fourier transformation of the data. At the higher field the signal was sufficiently strong to determine the mass from the second harmonic as well as from the fundamental. These two measurements are in good agreement with each other and are slightly smaller than the low-field value. Because interference effects are less serious at high field, we believe the high-field measurements are more reliable.

The masses for the β and γ open hole orbits can be compared directly to earlier measurements at two angles: γ at [011] and β at 76° from [100] in the $(01\bar{1})$ plane. In the former case, the agreement is within a few percent with the results of Windmiller *et al.* and Dye *et al.* In the latter case, the present measurement is 14% to 19% larger than reported by Dye *et al.* Because of interference problems at this angle as discussed in Sec. II B 1, an additional measurement was made at the nearby angle 77.6° where the frequencies are better separated. This measurement confirmed our result at 76° as shown in Fig. 2. Dye *et al.* also report measurements of the β and γ orbits at 63° from [100] in the $(01\bar{1})$ plane which can be compared with our measurement at 61.4° and with extrapolations of our mass data using a KKR parametrization (see Fig. 1 and the following paper). Their results for the β and γ orbits are 15% and 12% lower than ours, about the same discrepancy as at 76°.

As a final test of the validity of our higher values for the masses on the open hole sheet we measured the masses of the central and noncentral orbits on the Γ-centered electron sheet at 61.4° under the same conditions as used for the β and γ orbits at this angle, changing only the modulation amplitude in order to optimize the signal. Our results for the masses on the electron sheet are $\sim 2\%$ lower than those reported by Windmiller *et al.* [Fig. 12(d) of Ref. 32], indicating that the higher masses found on the open hole sheet cannot be due to systematic errors in the measurement procedure.

Since the work of Dye *et al.*, several improvements have been made in the signal-to-noise ratio and the maximum field available for the mass measurement has been increased from 12 to 15 T. In the present measurements, greater attention has been paid to interference problems and other sources of error as described in Sec. II B. The eight masses on the β and γ orbits reported here are consistent with each other and give a more complete picture of the mass variation on the open hole surface than do the four masses reported by Dye *et al.*

2. Field dependence

The masses shown in Table I are plotted in Fig. 4 as a function of magnetic field. The masses of the [100] and [010] orbits on the $X(1,0,0)$ pocket, which were taken on the same run, seem to show a reduction of 3% to 4% when the field is increased from 5.5 to 11.8 T. However, this reduction is within the error bars of the measurements. Furthermore, the mass of an orbit on the same pocket at an intermediate field direction shows no significant field dependence. On the Γ-centered electron sheet the mass of the [110] orbit shows no field dependence in a field range of 6.2 T.

On the open hole sheet the mass of the α orbit at [100]

TABLE I. Cyclotron effective masses in Pd measured at different magnetic field intensities.

FS sheet, orbit	Center ($2\pi/a$)	Field direction	Area (a.u.)	Field H (T)	Mass (m^*/m)
X holes	$X(1,0,0)$	[100]	0.0153	5.50	0.629±0.008
				11.81	0.606±0.016[a]
		22° from [100] in (01$\bar{1}$)	0.0158	5.68	0.665±0.025
				5.68	0.634±0.028[b]
				11.82	0.646±0.028[a]
		[010]	0.0238	5.50	1.067±0.011
				5.50	1.070±0.015[c]
				11.81	1.033±0.015[c]
Electrons	Γ	[011]	0.827	6.89	2.253±0.026
				13.13	2.267±0.023
	Γ	61.4° from [100] in (01$\bar{1}$) plane	0.646	13.84	1.936±0.020
	Λ[d]	61.4° from [100] in (01$\bar{1}$) plane	0.678	13.84	1.944±0.051
Open holes, α	$W(\frac{1}{2},0,1)$	[100]	0.0719	5.50	2.39 ±0.11
				11.81	2.22 ±0.04
				11.81	2.28 ±0.03[c]
		22° from [100] in (01$\bar{1}$)	0.0771	5.68	2.64 ±0.03
				11.82	2.60 ±0.03
Open holes, β	$X(1,0,0)$	61.4° from [100] in (01$\bar{1}$)	0.218	11.54	6.55 ±0.07
				13.19	6.68 ±0.08
		76° from [100] in (01$\bar{1}$)	0.240	11.09	9.35 ±0.41
				13.00	8.82 ±0.24
		77.6° from [100] in (01$\bar{1}$)	0.246	11.38	9.49 ±0.37
				13.25	9.18 ±0.20
Open holes, β'	$X(0,1,0)$	61.4° from [100] in (01$\bar{1}$)	0.252	11.54	7.83 ±0.15
				13.19	8.05 ±0.15
Open holes, γ	$S[011]$[d]	61.4° from [100] in (01$\bar{1}$)	0.282	11.54	9.71 ±0.47
				13.19	10.06 ±0.28
		76° from [100] in (01$\bar{1}$)	0.223	11.09	7.26 ±0.18
				13.00	7.09 ±0.29
		77.6° from [100] in (01$\bar{1}$)	0.217	11.38	6.95 ±0.11
				13.25	6.51 ±0.08
		[011]	0.202	9.82	5.80 ±0.07
				12.39	5.99 ±0.07

[a] Determined from the fourth dHvA harmonic.
[b] Determined from the third dHvA harmonic.
[c] Determined from the second dHvA harmonic.
[d] Non-central orbit.

shows an apparent field dependence due to the interference problems at low field as discussed above. A second measurement, performed 22° away where there is no interference, shows no field dependence. On the high-mass β and γ orbits, both the uncertainty and the scatter in the data are larger. The scatter favors positive and negative field dependences equally often; i.e., the masses measured at high fields are larger than those measured at low fields for exactly half the orbits measured. In order to account for a 7% reduction in the electronic specific heat at 10 T, the average mass on these orbits must decrease by 0.7% per T. A trend of this magnitude cannot be seen for any of the β or γ orbits. Furthermore, if there is any field dependence of the effective masses of these orbits we expect it to vary slowly with field direction. The scatter in Fig. 2 does not follow such a pattern; e.g., the measured field dependence of the mass on the γ orbit changes from positive to negative to positive in an angular range of $\sim 30°$ with an average field dependence of approximately zero. Given the relative sizes of the scatter and the uncer-

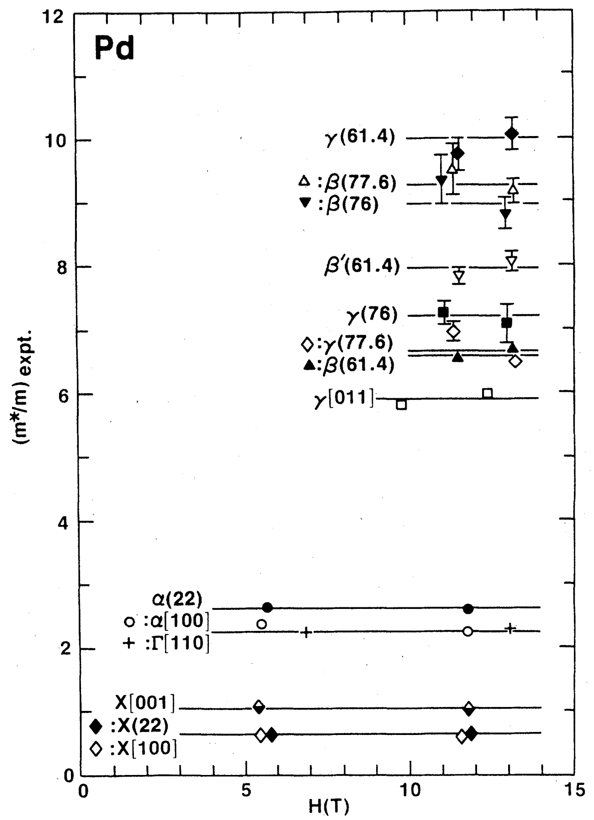

FIG. 4. Magnetic field dependence of the cyclotron effective masses shown in Table I.

tainty in the measurement we believe the data are most consistent with a field dependence of zero for all the masses.

B. Spin-splitting zero

An especially sensitive test for changes in the argument of the spin-splitting factor can be made at a spin-splitting zero, where the argument equals $(n+1/2)\pi$. Any change of the argument with field induces a change in the field direction at which the zero occurs. Because this method depends only on the detection of a zero in the signal, it is independent of all systematic errors affecting the measurement of field, temperature, frequency, and amplitude.

A search for field dependence in the argument of the spin-splitting factor was made at the only known zero of the fundamental dHvA signal on the open hole sheet. This zero occurs on the α orbit $\sim 17°$ from [100] as reported by Windmiller *et al.*[32] and Ohlsen *et al.*[37] Although the α orbit does not sample the very high density of states regions near the "fins" along the X-L line, its mass is significantly enhanced over the band-structure value[21] indicating that many-body effects are important for this orbit. The magnitude of the shift in the field direction of the zero depends on the anisotropy in the argument of the spin-splitting factor, which has recently been measured for the α orbit by Ohlsen *et al.*[37] Using their values for the anisotropy, a 2.5° shift away from [100] will occur for each radian by which the argument is reduced. Assuming the field dependences of γ_{el} and M/H occur by uniform scaling of all the orbital contributions, and that

$$(\Delta\gamma_{el}/\gamma_{el})/(\Delta\chi/\chi)=0.2$$

as observed for Pd(Ni) alloys,[31] then a reduction of about 3.5% per T is required in the argument of the spin-splitting factor in order to account for a 0.7% per T reduction in the specific heat. Using the estimate of Ohlsen *et al.* for the argument of the spin-splitting factor at its zero of $17\pi/2$, a shift of 14° in the orientation of the zero is expected when the field is increased by 6 T. Experimentally we observe the zero to shift from 17.4°±0.05° at 6 T to 17.3°±0.05° at 12 T. This shift is much smaller than expected based on the specific-heat measurement of Hsiang *et al.*, but is quite consistent with high-field magnetization experiments which show a slight *increase* in M/H at high fields. The measurements of Muller *et al.*[38] to 32.5 T imply that the zero should shift 0.04° toward [100] if the field is changed from 6 to 12 T (assuming the field dependence of M/H occurs by uniform scaling of all the orbital contributions), compared to the experimental result of 0.1°±0.05°. The tiny field dependence of the argument of the spin-splitting factor of the α orbit supports our conclusion that a magnetic field of 13 T does not affect the spin-fluctuation enhancements significantly.

IV. CONCLUSIONS

We have searched for evidence of spin fluctuations in Pd by measuring the cyclotron effective masses and the argument of the spin-splitting factor in the LK expression for the amplitude of the dHvA effect as a function of magnetic field. These two measurements probe the spin-fluctuation contribution to two different conduction-electron properties: the itinerant density of states at the Fermi level which determines the electronic specific heat, and the difference in volume between the spin-up and spin-down Fermi surfaces, which determines the itinerant spin magnetization.

The absence of significant field dependence in either the cyclotron effective masses or the argument of the spin-splitting factor implies that the spin-fluctuation contribution to the electronic specific heat and spin susceptibility M/H are not appreciably affected by applied fields up to 13 T. These results are consistent with theoretical estimates (Brinkman and Engelsberg,[16] Hertel,[17], Béal-Monod,[18] and Bedell[39]) that magnetic fields much larger than 13 T are required to suppress the spin fluctuations in Pd. Our results are also consistent with the fact that the spin-fluctuation enhancement of the electronic specific heat in Pd is rather small (Joss and Crabtree, following paper), so that a large suppression of the spin fluctuations would be required to produce a measurable reduction in the total electronic specific heat. Additional evidence favoring the field independence of spin fluctuations in Pd is provided by recent specific-heat experiments of Franse[23] up to 5 T and Stewart and Brand[24] up to 20 T which show no reduction in γ_{el} with field, and by a KKR parametrization of the new high-field masses reported here which predicts a density of states at the Fermi level differing from the zero-field specific-heat value by no more than 2.5% (Joss and Crabtree, following paper). All of this evidence taken together strongly supports the conclusion that a field of 13 T does not appreciably affect spin fluctuations in Pd.

Our results illustrate the problems of ascribing a field dependence in the specific heat to spin fluctuations without additional supporting evidence. Before such an interpretation can be made, it is necessary to show that the field dependence occurs in the conduction-electron system and is not associated with a local effect such as a magnetic impurity. The best evidence for field dependence in the conduction-electron system comes from a Fermi surface experiment like the dHvA effect. When such data are not available, the source of the field dependence can be investigated less directly through magnetization measurements. The signature of a local moment effect is more evident in magnetization data than in specific-heat data because the magnetization is not sensitive to the large phonon contributions which dominate the specific heat at most temperatures. Local magnetic effects like single-impurity paramagnetism, ferromagnetic clustering, spin-glass order, or Kondo effect are readily detectable with magnetization experiments. All of these local effects induce a field dependence in the specific heat which, under certain conditions, might be confused with spin fluctuations. In addition to revealing the existence of specific local moment effects in the sample, magnetization measurements can be used to quantitatively support a field dependence in the specific heat through the Maxwell relation[19]

$$\frac{\partial[C(H,T)/T]}{\partial H}=\frac{\partial^2 M(H,T)}{\partial T^2} .$$

A precise experimental determination of the right-hand side above is usually difficult because it involves taking a numerical second derivative, but semiquantitative estimates are possible, as have recently been given for $TiBe_2$ by Acker *et al.*[40] Careful magnetization measurements and verification of the Maxwell relation are important steps in characterizing the origin of a field dependence in the specific heat and showing that it is an intrinsic property of the sample.

Note added in proof. Recently Appel and Fay[41] have reexamined the spin-fluctuation effects on dHvA amplitudes and the electronic specific heat, taking into account the momentum dependence of the electron self-energy. They find that the same contribution appears in both the dHvA effective mass and the electronic specific heat, so that the properly averaged cyclotron effective masses should give the same enhanced density of states as would be derived from the electronic specific heat, even in the presence of spin fluctuations. This explicitly shows that a field dependence in the electronic specific heat must appear also in the cyclotron effective masses measured by the dHvA effect, a point we have implicitly assumed in our treatment.

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