Measurements of the conduction-electron g factor in palladium

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Measurements of the conduction-electron Zeeman splitting in palladium are presented. With the use of the de Haas–van Alphen effect the anisotropy of the orbit-averaged g factor has been mapped out in some detail for the Γ_6 sheet and the α orbit. A pronounced anisotropy was found for the Γ_6 sheet. Detailed studies of the spin-splitting zeros have revealed new contours and an angular dependence different from that previously reported.

I. INTRODUCTION

The magnetic properties of palladium have for a long time stimulated both experimental and theoretical works. In this paper we present an investigation of the Zeeman splitting of the conduction electrons in palladium as seen in the de Haas–van Alphen (dHvA) effect.

This technique gives an orbital g factor enlarged by a cyclotron Stoner enhancement[1] as described below. The absolute value of g_c cannot be estimated but its anisotropy can be obtained.

In the expression for the amplitude of the kth harmonic of the dHvA oscillations there is a cosine factor with the argument $k\pi R$, where $R=E_Z/E_L$, E_Z being the Zeeman splitting energy of the cyclotron orbit and E_L the Landau-level energy spacing. The argument can also be written as $k\pi g_c m_c/2m$, where g_c is the orbital g factor enlarged by the cyclotron orbit Stoner enhancement, m_c is the cyclotron effective mass, and m is the free-electron mass.

With dHvA spectroscopy a change by one-tenth of the cosine term is easily resolved. For a typical Landau-level spacing of 1 meV an energy resolution of 10^{-4} eV is achieved.

The easiest way to investigate the anisotropy of g_c is to map out spin-splitting zero (SSZ) contours over the Fermi surface (FS). A SSZ occurs whenever $\cos(k\pi R)=0$, that is, $kR=n+\frac{1}{2}$, where n is an integer. Between different neighboring contours on a FS sheet the value of n can be the same or differ by ± 1. This uncertainty can be resolved through studies of samples doped with magnetic impurities.[2] The integer n, however, cannot be determined by using the dHvA effect since it appears in the argument of a cosine function.

The SSZ method has been regarded as rather limited, since it only gives R along the SSZ contours. However, the method is powerful when several contours exist over the FS, as for example in platinum,[3,4] or over part of the FS, as in palladium. By studying SSZ's of higher harmonics of the dHvA frequencies additional information can be gained.

By measuring the amplitude and its variation between SSZ contours and by taking into account factors that affect the amplitude other than $\cos(k\pi R)$, it is possible to find the variation of R outside the SSZ contours. It is in fact possible to normalize the value of the fundamental amplitude since the cosine factor equals $1/\sqrt{2}$ whenever the second harmonic has a SSZ.[3]

There have been several calculations of the conduction-electron g factor. Both average values[5] and point g factors[6–8] show a notable deviation from the free-electron value and have a high anisotropy and a strong $\vec{k}$ dependence due to spin-orbit interaction. The anisotropy of the g_c factors in palladium has not been the object of a detailed experimental investigation even though Windmiller, Ketterson, and Hörnfeldt (WKH),[9] who were the first to report on SSZ contours in palladium, have demonstrated that such an anisotropy exists.

In this paper measurements of the anisotropy of the g_c factor of the closed Γ_6 sheet and the α orbit existing at the W point on the open hole sheet are reported. We have completely mapped out the SSZ contours for the fundamental frequency of the central orbit of the Γ_6 sheet, and for the first time SSZ contours of the off-central orbit of the Γ_6 sheet are reported. In the vicinity of [110] the SSZ contours of the central orbit differ substantially from the results of WKH. We have also investigated the variation of R in the symmetry planes (100) and (110).

For the α orbit the locations of the SSZ's in the mirror planes were determined and connected with the SSZ's observed by WKH to establish SSZ contours. The variation of R in the symmetry planes has also been established. We think our study constitutes a good basis for extended experimental investigations of the open hole sheet and the closed Γ_6 sheet and for stimulating calculations of the anisotropy of the g factor in palladium.

II. EXPERIMENTAL

The floating-zone technique, employing radio-frequency heating in argon atmosphere, was used to grow a palladium single-crystal rod.[10] The starting material was pure palladium powder with an impurity content of less than 4 ppm. A palladium crystal diluted with a small amount of nickel was also grown. A molten zone was passed several times in both directions along the diluted crystal in order to homogenize it.

The samples were then spark-cut from the single-crystal rod into a cylinder with length and diameter of about 1 mm and etched in aqua regia. The palladium sample was

annealed in air at 1300 K for 12 h. To remove the oxide coating resulting from the annealing process it was etched again. The amount of nickel in the diluted palladium sample was determined to 485 ± 10 ppm with a concentration gradient of less than 4% over the sample by using atomic absorption analysis of pieces of the single crystal cut from each side of the sample which was used in the dHvA measurements. Laue diffraction was used both to orientate the samples and to check the entire surface, since some samples showed a tendency to form twin crystals with small angular differences in orientation.

Even a very small amount of iron in palladium will drastically change the Stoner enhancement parameter,[11] thus changing the location of a SSZ. Therefore, it is essential that the palladium sample has a very low iron content. The excellent agreement of our results with the measurements of WKH (see Sec. III) indicates that the amount of iron in the pure palladium sample is extremely low. Low Dingle temperatures for both samples further confirm that they are of high quality.

The field-modulation technique has been used, and the measurements were carried out at a magnetic field of 6.5 T and at a temperature of 0.5 K. The experimental setup and the digital recording method are described in Ref. 4.

III. RESULTS

The occurrence of well-developed SSZ's of the dHvA amplitude is dependent on the quality of the sample as well as on the change of R with angle, $dR/d\theta$. The larger $dR/d\theta$ is, the more distinct the SSZ's will be. Since the Γ_6 sheet has a rather large change of R with angle over the whole sheet and our experimental setup gives an angular resolution of 0.1°, it was possible to determine the locations of the SSZ's on the fundamental within 0.2°. Owing to low signal amplitude and a small value of $dR/d\theta$ close to [100] on the α orbit, the uncertainty of the locations of the SSZ's is 0.3° in this case.

When studying higher harmonics of the dHvA frequency, a numerical analysis was used, giving an accuracy for the SSZ locations of 0.4°.

A. Γ_6 sheet

Figure 1 shows that our measurements of the locations of the SSZ's on the fundamental of the central orbit are in excellent agreement with the measurements of WKH. With the additional new data it is obvious, however, that the SSZ contours must be connected quite differently in the vicinity of [110] compared with the contours given by WKH. $\Gamma(1)$ is a closed contour surrounding [110], cutting through the (110) plane 1.6° out from [110] and 2.0° out in the (100) plane. $\Gamma(2)$ cuts through the (110) plane 4.1° out from [110] and 23.9° from [100].

In the vicinity of [111] the coexistence of the off-central and the central orbit appears as a beat pattern in the dHvA signal. Whenever a SSZ occurs on either orbit the beat pattern will vanish. By studying the frequency of the remaining signal it is possible to determine to which orbit the SSZ should be assigned. We have mapped out two

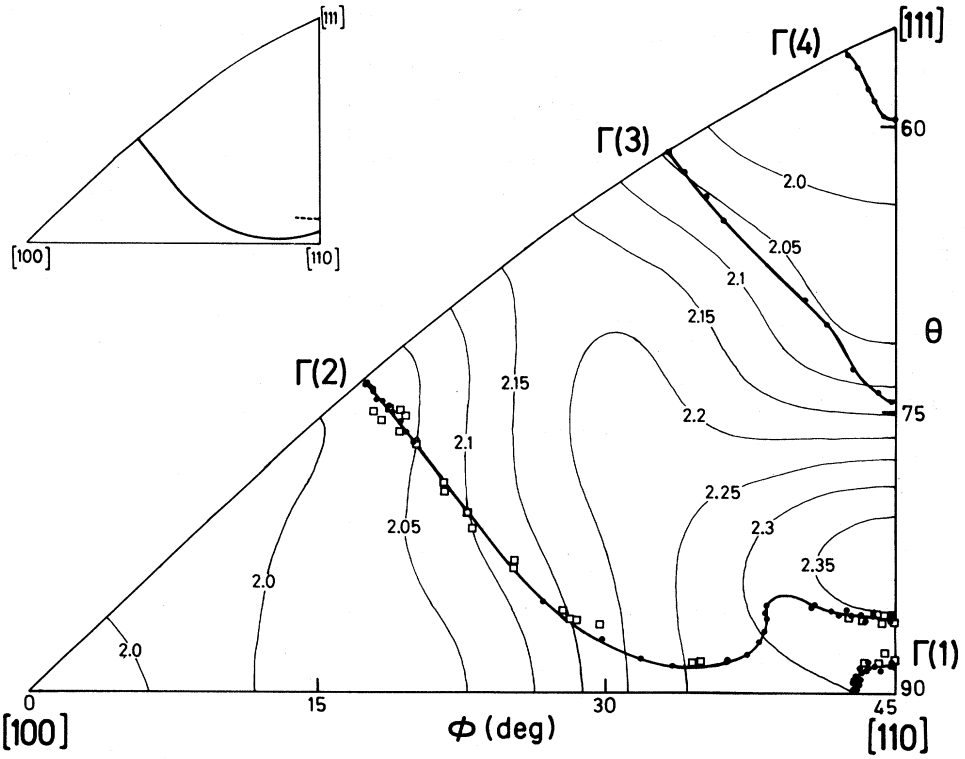

FIG. 1. Stereographic plot in the basic irreducible $\frac{1}{48}$th wedge of the Brillouin zone of the SSZ contours (heavy solid lines) on the Γ_6 sheet. Measurements of the SSZ's performed in this work are indicated by ● and those from WKH are indicated by □. The weak solid lines are contours of constant effective masses from WKH. The SSZ contours as presented by WKH are indicated in the small triangle in the upper left corner of the figure.

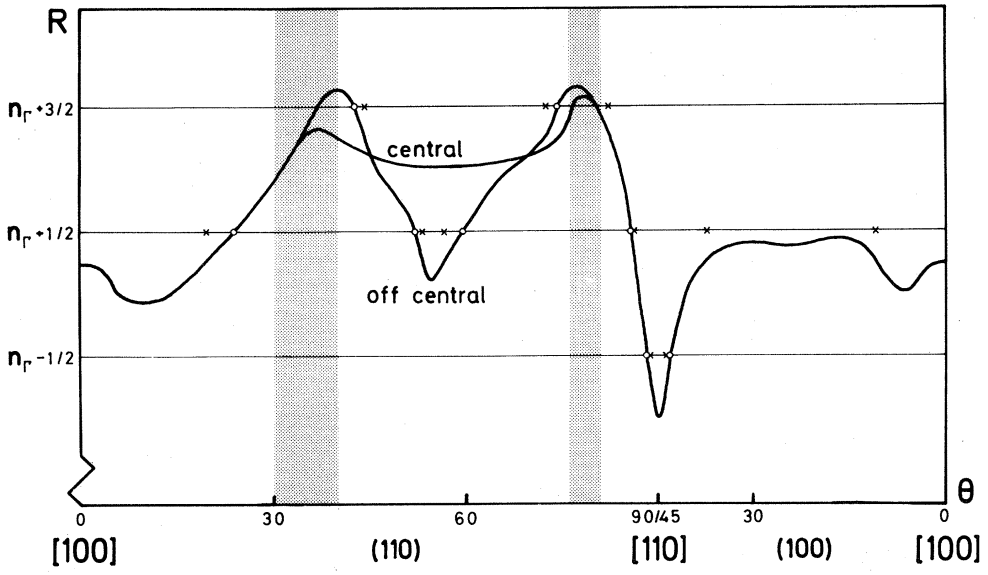

FIG. 2. $R(\theta)$ in the symmetry planes on the Γ_6 sheet. Shown also are our measurements of the SSZ's on the fundamental in palladium (○) and on the fundamental in the palladium sample diluted with nickel (×).

SSZ contours for the fundamental of the off-central orbit, and these are indicated in Fig. 1 by $\Gamma(3)$ and $\Gamma(4)$.

To determine whether the value of R is equal or changes by unity between the contours $\Gamma(1)$ and $\Gamma(2)$ and between $\Gamma(3)$ and $\Gamma(4)$, the locations of the SSZ's in the palladium sample doped with nickel were studied and compared with those of pure palladium. This was made under the assumption that the only effect of the nickel impurities in palladium is to shift $R(\theta)$ to higher values. These preliminary measurements[12] show that both $\Gamma(1)$ and $\Gamma(2)$ have moved closer to [110] and that $\Gamma(3)$ and $\Gamma(4)$ have moved closer to [111] when nickel is added. If we assign the values $n_\Gamma(2)+\frac{1}{2}$ and $n_\Gamma(3)+\frac{1}{2}$ to R for $\Gamma(2)$ and $\Gamma(3)$, respectively, the conclusion will be that R takes the values $n_\Gamma(2)-\frac{1}{2}$ and $n_\Gamma(3)-\frac{1}{2}$ for $\Gamma(1)$ and $\Gamma(4)$, respectively.

In order to obtain the variation of $R(\theta)$ on the Γ_6 sheet, the SSZ's in both the pure and the doped palladium sample were used as fix points. In those parts of the FS where SSZ's are frequently occurring, the magnitude of the shift of $R(\theta)$ caused by the nickel impurities as well as the slope of R, $dR/d\theta$, at each SSZ can be extracted and by also considering the measured amplitudes of both samples the variation of $R(\theta)$ can be established. In the areas close to [100] and [111] for the central orbit where there are no SSZ contours (see Fig. 1) the factors affecting the amplitude such as the effective mass and the curvature factor must be especially considered. The difference in Dingle temperature between the two samples was found to be small and was neglected. Studies of SSZ's of the second harmonic in these areas were made but the interpretation was difficult mainly due to the limited magnetic field strength and a strong influence from the X pockets on the dHvA signal. The best fit of $R(\theta)$ in the symmetry planes for palladium is presented in Fig. 2. The shaded parts in this figure represent the regions where the noncentral orbit splits off from the central orbit. No study of the amplitude has been performed in these regions since the beat pattern becomes too long to be measured accurately. Since in this region the central and off-central orbits are close to each other on the FS, the difference in the g_c factor for the two orbits should be small, thus leading to the conclusion $n_\Gamma(3)=n_\Gamma(2)+1$ as can be seen in Fig. 2.

In the vicinity of [111] the amplitude of the central orbit monotonically increases towards [111] both for the pure and doped palladium samples. A comparison of the amplitudes out from [111] relative the amplitude at [111] in the two samples shows that the downward bend for the graph of $R(\theta)$ is the most likely choice. To reveal a more detailed description of the variation of $R(\theta)$ for the central orbit in the regions near [100] and [111] an investigation of the SSZ's of the second harmonic or a more extended study of SSZ's in palladium samples with different amounts of nickel must be performed. To summarize, we find that the values of R, with $n_\Gamma(2)=n_\Gamma$, for the different SSZ contours are as follows:

$$\Gamma(1):\ R=n_\Gamma-\tfrac{1}{2},$$

$$\Gamma(2):\ R=n_\Gamma+\tfrac{1}{2},$$

$$\Gamma(3):\ R=n_\Gamma+\tfrac{3}{2},$$

$$\Gamma(4):\ R=n_\Gamma+\tfrac{1}{2}.$$

B. α orbit

Several SSZ's in the symmetry planes for the fundamental of the dHvA frequency on the α orbit have been established. Together with the results from WKH these can be used to complete three SSZ contours, which are shown in Fig. 3. A few SSZ's further out from [100] in the symmetry planes indicate the existence of additional SSZ contours.

$R(\theta)$ in the symmetry planes for the α orbit is presented in Fig. 4. The same analysis procedure as outlined

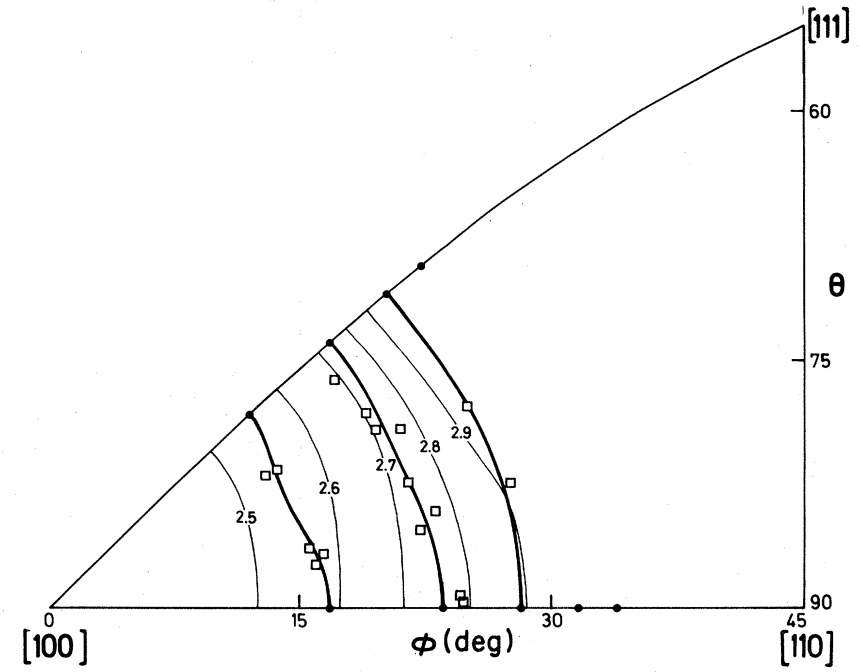

FIG. 3. Stereographic plot in the basic irreducible $\frac{1}{48}$th wedge of the Brillouin zone of the SSZ contours (heavy solid lines) on the α orbit. Measurements of the SSZ's performed in this work are indicated by ● and those from WKH are indicated by □. The weak solid lines are contours of constant effective masses from WKH.

above for the Γ_6 sheet has been used. Preliminary measurements on the dilute palladium sample[12] show that the value of R increases by unity for every successive SSZ contour with increasing distance from [100].

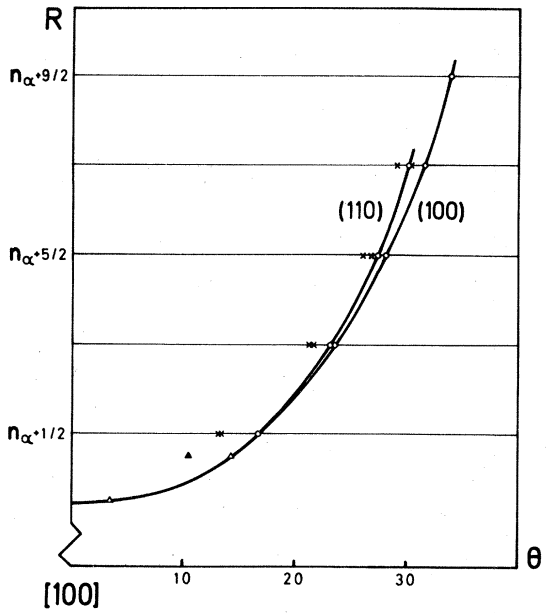

FIG. 4. $R(\theta)$ in the symmetry planes on the α orbit. Shown are also our measurements of the SSZ's on the fundamental and second harmonic in pure palladium indicated by ○ and Δ, respectively, and on the fundamental and second harmonic in the palladium sample diluted with nickel indicated by × and ▲, respectively.

IV. DISCUSSION

A. Γ_6 sheet

The absolute difference between the minimal and maximal value of R for the Γ_6 sheet is of the same order of magnitude in palladium and platinum. This is also valid for the variation of the g_c values since the effective masses are similar. The average Stoner factor in palladium is larger than in platinum, and if the cyclotron Stoner enhancement of the Γ_6 sheet is also larger in palladium the anisotropy of the g_c factors, not including the exchange enhancement, is less in palladium than in platinum. The indications in the calculations by Mueller *et al.*[6] are in agreement with this qualitative estimate.

SSZ's for the off-central orbit have not been reported earlier. The two contours presented in this work show that the part of the Γ_6 sheet which this orbit is scanning has a strong variation of its point g factors. Point g factors are here used as a measure of spin splitting of individual Bloch states perturbed by a magnetic field. Such a point g factor may be anisotropic with respect to the magnetic field direction and thus exhibit tensor properties.[13]

Knowledge of the effective masses[9] gives that g_c decreases by 13% when going across the irreducible $\frac{1}{48}$th wedge of the Brillouin zone along the $\Gamma(2)$ contour toward [110]. It is noticeable that R increases by 2 when going 6° out from [110], across $\Gamma(1)$ and $\Gamma(2)$, in the (110) plane. This change cannot be explained by the variation of m_c but must originate from an anisotropy of g_c. Thus g_c is increasing by roughly 1.5 in only 6°. This high anisotropy in the vicinity of [110] is similar to that found in platinum.[4]

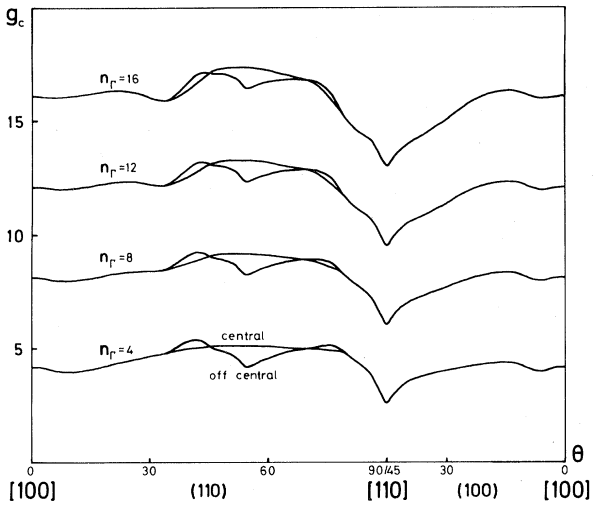

FIG. 5. g_c vs θ extracted from our $R(\theta)$ curve. Since n_Γ is not known, we present a set of g_c curves with different n_Γ. The effective-mass values for the off-central orbit are reported by WKH for only a few angles near [111] but they show a small deviation from the values for the central orbit. The effective masses for the central orbit have therefore been used to calculate g_c for both orbits.

Figure 5 shows that the choice of the integer n_Γ only has a minor effect on the variation of g_c with angle. All values of n_Γ given in the figure result in a pronounced dip in the graph at [110]. This direction represents a cyclotron orbit that passes over four [111] bumps. The dip can be correlated to the change in the wave-function character at these bumps. The Γ_6 sheet has a severe *s-d* hybridization, but in some directions such as [100] and [111] there is high *s*-electron content.[6,14] As in platinum, a high anisotropy of g_c could therefore also be expected at [100], where four [100] bumps are passed by the cyclotron orbit. We have, however, observed very low anisotropy in this region. The assumption of a low value of the point *g* factor at [111] also explains the dip in the g_c graph 35° out from [100] in the (110) plane for higher values of n_Γ. Here the cyclotron orbit passes over two [111] bumps. The fact that the dip is so much smaller here may be a result of the tensor nature of *g*. The cyclotron orbit of the off-central orbit is moving up on three [111] bumps when tilting the magnetic field toward the [111] direction. This may explain the extremely low local value of R in this direction.

Recently Jarlborg and Freeman presented high-field calculations of isotropic point *g* factors for palladium.[8] An exchange-correlation potential is included which should give *g* factors comparable in magnitude with the Stoner enhanced *g* factors reported here. These calculations reveal a strong $\vec{k}$ variation and an average of the *g* factors well above 5. They have found a low value of *g* at [100] and a high value at [111] for the Γ_6 sheet. Their results are not directly consistent with our measurements. This may be due to that isotropic point *g* factors do not give a relevant description of *g* factors or that an interpretation of the cyclotron orbit *g* factor as an average of the contributing Bloch-state point *g* factors is not straightforward.

B. α orbit

For any reasonable choice of n_α the major part of the anisotropy of R can be assigned to the anisotropy of m_c, and thus a rather isotropic g_c factor is obtained for the α orbit. A similar behavior was found in platinum.[3]

Along the SSZ contours the change in g_c can be calculated without knowledge of the value of n_α. Along each one of the three contours closest to [100], where the effective masses are known from WKH, the change in g_c is only 3%. For n_α between 7 and 20 the g_c factor will change by less than 8% when going up to 20° out from [100].

An isotropic g_c factor may be interpreted as a consequence of a more uniform *d*-like character for that part of the open hole sheet where the α orbit is existing although, generally, the open hole sheet is strongly affected by spin-orbit interaction. Mueller *et al.*[6] have calculated point *g* factors for this sheet, and the values obtained are generally higher than 2. The values are in the range $0.49 < g < 2.63$ and in good quantitative agreement with those calculated by Rahman *et al.*[7] The calculations by Jarlborg and Freeman[8] give point *g* factors for the open hole sheet that are fairly constant around 6.4. If this is valid also for the cyclotron orbit *g* factor, it would give $R = 7.7$ at [100] for the α orbit, which agrees well with the measured R (Fig. 4) if one assigns the value 8 to n_α.

The cyclotron orbit *g*-factor measurements can be seen as an extension of the dHvA technique as an experimental probe for investigations of electrons at the FS. In the same way that early dHvA measurements of extremal areas stimulated band-structure calculations, we hope that the *g*-factor measurements will lead to theoretical studies of wave functions for the Bloch states and of how they influence the Zeeman splitting. Comparison between the studies of palladium and platinum may then also reveal to what extent many-body effects are of importance for the anisotropy of the g_c factor, since a greater influence can be expected in palladium than in the heavier element platinum.

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