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G. Goll[1], J. Hagel[1], H. v. Löhneysen[1](*), T. Pietrus[1], S. Wanka[1], J. Wosnitza[1], G. Zwicknagl[2], T. Yoshino[3], T. Takabatake[3] and A. G. M. Jansen[4]

[1] *Physikalisches Institut, Universität Karlsruhe - D-76128 Karlsruhe, Germany*
[2] *Institut für Mathematische Physik, TU Braunschweig D-38106 Braunschweig, Germany*
[3] *Department of Quantum Matter, ADSM, Hiroshima University Higashi-Hiroshima 739-8526, Japan*
[4] *Grenoble High Magnetic Field Laboratory, MPI-Festkörperforschung and CNRS - F-38042 Grenoble, France*

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Abstract. – Shubnikov-de Haas (SdH) and Hall-effect measurements of CeBiPt and LaBiPt reveal the presence of very small Fermi surfaces with hole-like charge carriers for both semimetals. Reasonable agreement with band structure calculations is achieved when taking spin-orbit coupling into account and assuming localized Ce $4f$ electrons. For CeBiPt, we observe a strong temperature dependence of the SdH frequency, *i.e.*, an increase from $\sim 35\,\mathrm{T}$ at $10\,\mathrm{K}$ to $\sim 60\,\mathrm{T}$ at $0.4\,\mathrm{K}$, indicating a possible hybridization of the f electrons.

The Shubnikov-de Haas (SdH) effect, *i.e.*, quantum oscillations in the magnetoresistivity $\rho(B)$, was discovered more than 70 years ago in the semimetal Bi [1]. Since then, measurements of the SdH effect and the related de Haas-van Alphen (dHvA) effect in the magnetization have been successfully exploited to gain valuable information on the band structure parameters of many metals, semimetals, and complex materials with strong electron correlations such as heavy-fermion systems [2]. The oscillations are periodic in $1/B$ and the frequency F is directly proportional to the extremal cross-section A of the Fermi surface perpendicular to the magnetic field, *i.e.*, $F = (\hbar/2\pi e)A$. The theory of the dHvA effect is well established [3], and also the SdH effect, reflecting the more involved transport properties, is principally understood [4]. In many cases, the effective mass of the carriers in a given band of the Fermi surface can be determined from the temperature dependence of the amplitude of the oscillations. Here we report on a new observation, namely a strongly temperature-dependent *frequency* of the SdH oscillations. This anomalous T-dependence of F was found for a certain field orientation in semimetallic CeBiPt, while it is absent in the homologous —except for

(*) Also at Forschungszentrum Karlsruhe, Institut für Festkörperphysik - D-76021 Karlsruhe, Germany.

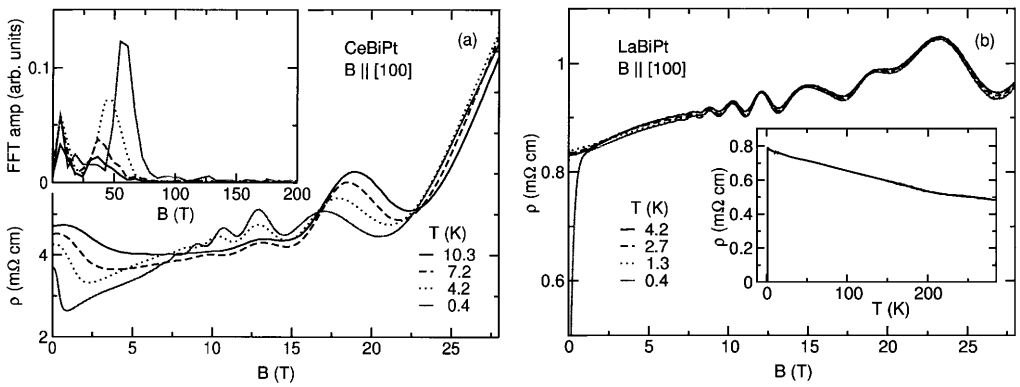

Fig. 1 – Field dependence of the resistivity ρ of CeBiPt (a) and LaBiPt (b) for selected temperatures. The inset in (a) shows the Fourier spectra of the SdH signals of CeBiPt. The inset in (b) shows the temperature dependence of ρ of LaBiPt with the superconducting transition at about 0.88 K.

the Ce $4f$ electron— semimetal LaBiPt. Relativistic band structure calculations, by use of the local-density approximation, reveal a strong sensitivity of the Fermi surface of CeBiPt to the admixture of itinerant $4f$ states, which suggests a possible temperature-dependent hybridization of the $4f$ electrons. The single crystals were grown at Hiroshima University with the Bridgman technique in a hermetically sealed Mo crucible from the starting materials Ce ($m5N$, Ames Laboratory), Bi ($m5N$), Pt ($m3N$), and La ($m4N$). To avoid oxidation of elemental Ce or La during handling, CePt or LaPt were first prepared by argon-arc melting and the appropriate amount of Bi was then added for single-crystal growth. The crucible, sealed under Ar atmosphere, was heated to 1350 °C with an intermediate halt at 500 °C for 2 h and after 12 hours was slowly cooled by moving it out of the central zone of the furnace with 1 mm/h. Whether the 1-1-1 compounds or 3-4-3 compounds like $Ce_3Bi_4Pt_3$ are formed depends very sensitively on the excess amount of Bi. The obtained 1-1-1 single crystals show the $F\bar{4}3m$ cubic structure previously determined for polycrystalline samples [5]. The lattice constant 6.8338 (25) Å found for CeBiPt is in good agreement with the previously reported value [5]. For the LaBiPt crystal, Laue-diffraction pictures showed some mosaicity of the sample, while no mosaicity could be detected for the CeBiPt samples [6]. The longitudinal (ρ_{xx}) and transverse (ρ_{xy}) magnetoresistance (Hall effect) were measured by use of ^{3}He cryostats up to 15 T in Karlsruhe, and up to 28 T at the High Magnetic Field Laboratory in Grenoble. In each case, the sample was securely glued with IMI7031 varnish to a Cu sample holder which was attached to the ^{3}He tank. Both sets of data agree perfectly with each other in the region of overlap, indicating that erroneous sources of our observations such as reorientation of the sample in the magnetic field can be ruled out. In addition, we checked the reproducibility of our results on two different CeBiPt samples. Six gold wires were glued with graphite paste to the samples, thereby enabling to measure ρ_{xx} and ρ_{xy} simultaneously. These resistances were measured by use of a low-frequency ($\sim$ 16 Hz) lock-in technique for normal and reversed field orientations which allowed a well-defined separation of ρ_{xx} and ρ_{xy}. The dHvA signal of the LaBiPt sample was measured by means of a capacitance cantilever torque magnetometer. All sample holders could be rotated *in situ* around one axis.

Figures 1(a) and (b) show the magnetoresistance $\rho(B)$ with B aligned along [1 0 0] for CeBiPt and for LaBiPt for several temperatures. The current direction was perpendicular to B. In both cases, clear oscillations are seen. For LaBiPt at $T = 0.4$ K, the strong decrease of ρ

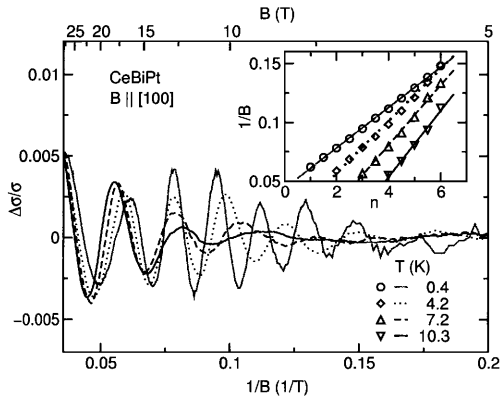

Fig. 2 – Field dependence of the SdH signal, *i.e.*, the relative conductance oscillations, of CeBiPt for different temperatures. The inset shows the peak and valley positions *vs.* an arbitrary index n.

to zero below about 1 T (with a mid point at 0.45 T) indicates the onset of superconductivity with $T_c = 0.88\,\mathrm{K}$ in $B = 0$ (see inset of fig. 1(b) for $\rho(T)$). For some field directions we observed a beat pattern in the SdH (but not in the torque) signal for LaBiPt which might be attributed to the mosaicity mentioned above.

For CeBiPt, a first unusual observation is the sharp drop of the magnetoresistance at low fields and low temperatures (fig. 1(a)). Below about $T_N = 1\,\mathrm{K}$, CeBiPt orders antiferromagnetically, as was evidenced by specific-heat and magnetization measurements for our samples [7, 8]. Recent neutron-scattering data have revealed a commensurate antiferromagnetic order with a wave vector $\boldsymbol{Q} = (1\,1\,0)$ [9]. Below T_N, the field-dependent magnetization, M, has a maximum in $\mathrm{d}M/\mathrm{d}B$ at about 0.3 T [7]. Therefore, the negative magnetoresistance at low fields presumably is caused by antiferromagnetic fluctuations which become reduced in an applied magnetic field.

The most striking observation for CeBiPt is the change of the SdH oscillation frequency with temperature. This can be made more apparent when the resistivity is converted to conductivity via $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$ making use of the simultaneously measured transverse magnetoresistance ρ_{xy} [10]. A smooth background conductivity $\sigma_0(B)$ was fitted to the σ_{xx} data to obtain the SdH signal $\Delta\sigma/\sigma_0 = (\sigma_{xx} - \sigma_0)/\sigma_0$ as shown in fig. 2 *vs.* $1/B$. The oscillations are indeed periodic in $1/B$ within our resolution. The oscillation frequency F is directly obtained from the slope of $1/B$ *vs.* oscillation index n (inset of fig. 2). F decreases from 58.2 T at 0.4 K to about 35 T at 10.3 K (see fig. 3). The total change of F between 0.4 and 10.3 K corresponds to an apparent reduction of the Fermi-surface cross-section by more than 50%!

The anomalous T-dependence of F is found only for the field along the [1 0 0] and [0 1 0] directions where F is found to be about 58 T for $T \to 0$. Between approximately $\Theta = 20°$ and 70°, where Θ is the angle from the [1 0 0] direction toward [0 1 0], F is constant at 30 T and furthermore independent of T as shown in fig. 3 for B along the [1 1 0] direction. For B along the [1 1 1] direction a very low SdH frequency of about 20 T —but again independent of T— is found. The SdH and the dHvA frequencies for LaBiPt are T-independent and somewhat larger (65 T for B along [1 0 0] increasing to 95 T for B along [1 1 0]) than for CeBiPt. The large magnetization of CeBiPt due to the Ce $4f$ electrons prevented us from taking dHvA data for this compound. We emphasize that for both materials we were able to observe a SdH

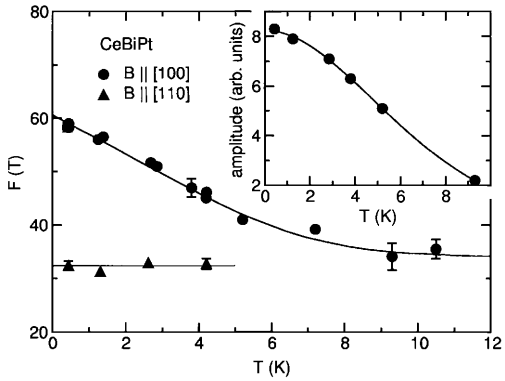

Fig. 3 – Temperature dependence of the SdH frequency of CeBiPt for two different field orientations. The lines are guides to the eye. The inset shows the temperature dependence of the SdH oscillation amplitude for $B \approx 10.5\,\mathrm{T} \parallel [1\,0\,0]$ with the fit for an effective cyclotron mass of $m^* = 0.24 m_\mathrm{e}$.

signal over the whole angular range. This suggests that the Fermi surfaces are simple singly connected hole pockets. The volume enclosed by the Fermi surface is estimated to comprise only about 1.5×10^{-4} of the volume of the first Brillouin zone for CeBiPt. This is consistent with the low (hole-like) charge carrier concentration n_h. Within a free-electron picture, n_h corresponds to a Fermi energy of $E_\mathrm{F} = \hbar^2(3\pi^2 n_\mathrm{h})^{2/3}/2m^* = 12.8\,\mathrm{meV}$. Assuming a circular Fermi-surface cross-section $A = \pi k_\mathrm{F}^2$ with the Fermi wave vector k_F, this results in a SdH frequency of $F = m^* E_\mathrm{F}/\hbar e \approx 27\,\mathrm{T}$, in nice agreement with the experimental F between 20° and 70° as well as for $B \parallel [1\,0\,0]$ at higher T.

The inset of fig. 3 shows the decrease of the amplitude A of the SdH oscillations with increasing T as measured for the oscillation around 10.5 T. We note, however, that the T-dependence of A is anomalous at higher field, *i.e.*, at 15–22 T it *increases* with increasing T (see fig. 2) in contradiction to standard theory [11].

Nevertheless, the T-dependence of A at $\sim 10.5\,\mathrm{T}$ can be described quite well with the standard expression $A \propto T/\sinh[\alpha(T/B)(m^*/m_0)]$, with $\alpha = 2\pi^2 k_\mathrm{B} m_0/e\hbar = 14.69\,\mathrm{T/K}$ [11]. We obtain the effective mass $m^* = 0.24\,m_0$, where m_0 is the free-electron mass. For $B \parallel [1\,1\,0]$ where F is independent of T (cf. fig. 3), we find the standard T-dependence of A for the *whole* field range, yielding $m^* \approx 0.3 m_0$. A simple consistency check serves to test whether we are indeed dealing with a quantum-oscillation phenomenon. From the field dependence of $\Delta\sigma/\sigma_0$ at fixed T we estimate [11] an average charge carrier scattering rate $\tau^{-1} = 3.3 \times 10^{12}\,\mathrm{s}^{-1}$. Together with the carrier density $n_\mathrm{h} = 7.7 \times 10^{17}\,\mathrm{cm}^{-3}$ obtained from the Hall effect at liquid-He temperature, we obtain in the simple Drude model $\rho \approx 3.7\,\mathrm{m\Omega\,cm}$ which is perfectly in line with the measured resistivity. One might argue that the anomalous B-dependence of A is the result of a beating pattern. The fast Fourier transforms (FFTs) of the SdH data reveal broad peaks, which clearly shift with temperature (inset of fig. 1(a)). A fit of the SdH signal at low T indeed is possible with two SdH frequencies which, however, are well within the width of the FFT peak. Further on, even with the assumption of different effective masses, while compatible with the low-T behavior, we cannot account for the observed SdH signal at higher T. Rather, a shift of *both* frequencies has to be invoked in order to explain the data.

The main point of the present investigation is the observation of a T-dependence of the quantum-oscillation *frequency* which is found only for the Ce-based metal. To our knowledge an effect of this magnitude has never been observed before. A small frequency change of the

order of $(k_{\mathrm{B}}T/E_{\mathrm{F}})^2$ may be expected [11] but would amount to only $\sim 10^{-3}$ between $T = 0$ and 5 K, much too small to account for our observation. We also checked by elastic neutron scattering that the lattice constant changes by only about 1% between room temperature and 1.45 K, ruling out large thermal-expansion effects. Another possible origin for this behavior would be a temperature-dependent charge carrier density which would lead to a Fermi-surface change. However, the simultaneously measured Hall constant, $R_{\mathrm{H}} = 1/n_{\mathrm{h}}e$, is independent of temperature.

One important fact which is evident from our investigation is the absence of any unusual effect for the non-magnetic sister compound LaBiPt. Therefore, it is clear that the magnetism of the Ce atoms affects the magnetic quantum oscillations. A trivial effect causing the anomalous T-dependence of the SdH frequency F would be a corresponding large field and temperature-dependent background magnetization M, since the SdH signal is proportional to $\sin(2\pi F/B_i)$, where the magnetic induction $B_i = \mu_0(H + M)$ is different from the externally applied field $B = \mu_0 H$. However, in order to explain the experimentally observed increase of F with decreasing temperature, M would have to become smaller at lower T, contrary to what we observe (data not shown). Moreover, the magnitude of $\mu_0 M$ compared to B is much too small to account for the observed change of F.

Having excluded all of the above more conventional scenarios, it is worthwhile to compare our findings with recent own and previously published [12] relativistic band structure calculations. Both of these calculations reveal the importance of spin-orbit coupling, *i.e.*, only for a fully relativistic treatment of the problem both LaBiPt [12] and CeBiPt are found to be

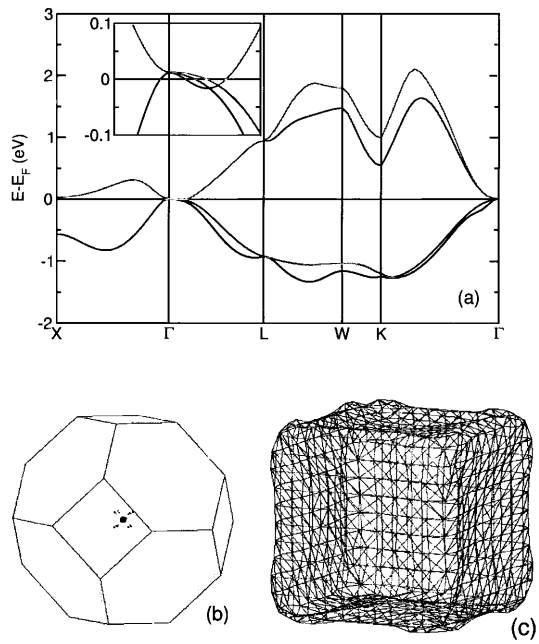

Fig. 4 – (a) Dispersion relation of the energy bands in CeBiPt intersecting the Fermi energy E_{F} calculated for localized $4f$ states. The inset shows the interesting region close to Γ in an enlarged scale. (b) Calculated Fermi surfaces in the fcc Brillouin zone. Very small electron-like surfaces surround two central hole-like Fermi surfaces. (c) Enlargement of one of the hole-like Fermi surfaces [13].

semimetals, otherwise semiconducting behavior would result. For LaBiPt very small hole and electron pockets are predicted [12]. The calculated (two) hole-like Fermi surfaces have exactly the observed topology, *i.e.*, angular dependence of the Fermi-surface cross-section (not shown) with an only slightly (by 20%) overestimated absolute value. Considering the smallness of the Fermi surfaces this agreement is excellent. Equally satisfactory is the agreement between the calculated (m^* between 0.11 and $0.21m_0$) [12] and measured ($m^* = 0.17m_0$) effective masses.

For CeBiPt, the only principal difference are the additional $4f$ electrons which either might be localized or itinerant. The results of relativistic band structure calculations by use of the local-density approximation assuming localized f states are shown in fig. 4. The validity of the resultant band structure was carefully checked by two independent algorithms. Details of the calculation will be published elsewhere. The gross features of the band structure are very similar to the LaBiPt results. Around Γ two small hole-like Fermi surfaces of area similar to that measured are predicted [13]. Further on, a number of very small electron-like pockets are obtained which seem to be too small to be experimentally observable. Interestingly, the Fermi-surface topology changes completely when itinerant $4f$ electrons are assumed. A complicated multi-connected Fermi-surface monster would result (not shown), which would be entirely at odds with experiment. Consequently, the calculated dispersion relation and the Fermi surface of CeBiPt (fig. 4) depend very sensitively on the admixture of itinerant $4f$ states. Therefore, the band structure calculations in connection with the experimental findings, *i.e.*, the Fermi-surface topology as well as the small specific-heat Sommerfeld coefficient [7], clearly prove the localized character of the $4f$ electrons.

This exceptional sensitivity of the band structure on the character of the $4f$ electron states suggests a possible explanation for the observed temperature-dependent Fermi surface. The band structure calculations show that the Fermi-surface cross-section for B along [1 0 0] is especially susceptible to the admixture of $4f$ states which is in line with the changes of F we observed only for this field direction. Consequently, this change might be a signature of an increasing hybridization of the $4f$ electrons with decreasing temperature. The special band structure with bands which barely cross the Fermi energy are responsible for the unique sensitivity of CeBiPt to hybridization effects.

In summary, we have presented an unusual T-dependence of magnetic quantum oscillations in CeBiPt which is due to the magnetic Ce $4f$ electrons as evidenced by the absence of this effect in LaBiPt. The obtained band structure parameters fit nicely with quantities obtained from other measurements and are in good agreement with fully relativistic band structure calculations assuming localized $4f$ electrons for CeBiPt. The sensitivity of the Fermi-surface topology to the amount of $4f$ hybridization suggests a possible temperature-dependent change of the itinerant character of the $4f$ electrons. However, further theoretical work is needed to unravel the origin of this unusual phenomenon.

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