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Shubnikov–de Haas oscillations in intercalation compounds of $2H$-TaS$_2$

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We report the first observation of the Shubnikov–de Haas effect in hydrated metal intercalation compounds of $2H$-TaS$_2$. Electrochemically intercalated samples of $K_x(H_2O)_yTaS_2$ show oscillations in the magnetoresistance for the single-phase compounds $(0.27 < x < 0.4)$ at magnetic fields higher than about 8 T. Several oscillations with frequencies smaller than 180 T are found in all samples investigated. The samples with $x = 0.295$ to $x = 0.33$ show also two higher frequencies of about 355 and 850 T. The effective masses of these two orbits are 1.0 and 1.2, respectively. The data cannot be described by a simple rigid-band model.

The intercalation compounds of the transition-metal-dichalcogenides $2H$-MX_2 (M=Nb,Ta and X=S,Se) are model compounds for quasi-two-dimensional metals and superconductors.[1] It was shown that the critical field H_{c2} undergoes a transition from three-dimensional to two-dimensional behavior upon lowering the temperature.[2,3] This quasi-two-dimensional behavior should also be seen in the Fermi surfaces of these compounds. Therefore, it is of interest to study in these crystals effects like magneto-oscillations to determine the Fermi surfaces. To our knowledge until now nobody has succeeded in finding magneto-oscillations in these intercalation compounds. Even in the undistorted binary compounds (e.g., NbS$_2$) no oscillations have been reported. The only experimental data available are Shubnikov–de Haas (SdH) and de Haas–van Alphen oscillations in the charge-density wave (CDW) phase of the $2H$ forms of NbSe$_2$, TaSe$_2$, and TaS$_2$.[4,5]

We have shown earlier[6] that electrochemical intercalation in aqueous solution of potassium into TaS$_2$ yields crystals of high quality (residual resistance ratios between 20 and 40). The chemical formula of these compounds is $K_x(H_2O)_yTaS_2$. In this paper we report the first observation of SdH oscillations in these crystals; the oscillations are seen at fields higher than 8 T. Of special interest is the ability of varying the potassium content x from $x = 0.27$ to 0.4 by electrochemical preparation. Since the potassium ion is fully ionized (Silbernagel[7] has shown that this is true even for the nonhydrated Li intercalation of compound LiTaS$_2$) there is a charge transfer xe_0 per formula unit of TaS$_2$, where e_0 is the electron charge. We can thus investigate the filling up of the TaS$_2$ bands in this regime.

$2H$-TaS$_2$ was prepared by a conventional vapor phase transport reaction at 900 °C via the $1T$ form and a subsequent annealing procedure. The residual resistance ratios of these crystals were typically between 50 and 80. Before intercalation the crystals were cut by a razor blade into a rectangular form ($\sim 2\times 5$ mm^2). The weights of the crystals were about 1 mg. The intercalation process was carried out by an electrochemical technique in deaerated saturated aqueous solutions of KNO$_3$. The intercalation time was about 150 min. The chemical formula of the intercalated compound can be written as $K_x(H_2O)_yTaS_2$. One obtains single-phase compounds for $0.27 < x < 0.4$. The H$_2$O content y can be roughly calculated from the formula $x + y = 1$. The layer separation induced by the intercalation amounts to 0.3 nm.[8] After intercalation the crystals were mounted within 15 min for a four-probe measurement of the in-plane resistivity. Electrical contacts were made by gold paint; care was taken to produce a homogeneous current distribution. The samples were cooled down to 4.2 K within 5 min to avoid loss of the cointercalated H$_2$O. The measurements were carried out at the Grenoble high-field facility B6 (Bitter-type magnet). The highest attainable field was 20 T; the temperature could be varied from 4.2 to 1.35 K. The crystal c axis was mounted parallel to the magnetic field. Two experiments were done using a sample holder with a rotation capability.

All intercalation compounds investigated showed a high residual resistance ratio of 20 to 40 and became superconducting at temperatures below 5.5 K. We have performed magnetoresistance measurements for samples with nominal stoichiometry $x = 0.28$, 0.295, 0.31, 0.33, 0.347, 0.362, and 0.38. For $x = 0.33$ we measured three different samples, for $x = 0.28$ two samples. The results were highly reproducible. The magnetoresistance at 20 T is in the range of 20–40 % of the resistance at $B = 0$ T (above the superconducting transition). Oscillations of the magnetoresistance can be seen only for fields higher than about 8 T depending on the sample. At 20 T the oscillatory part of the magnetoresistance amounts to 10–40 % of the normal magnetoresistance. A typical example of SdH oscillations for a sample with $x = 0.33$ is shown in Fig. 1. The upper part (a) was measured at a temperature of 4.2 K, the lower part (b) at $T = 1.4$ K. We performed Fourier transform analyses of all our data (after subtracting a straight line fitted to the magnetoresistance curve). In Fig. 2 we show the Fourier trans-

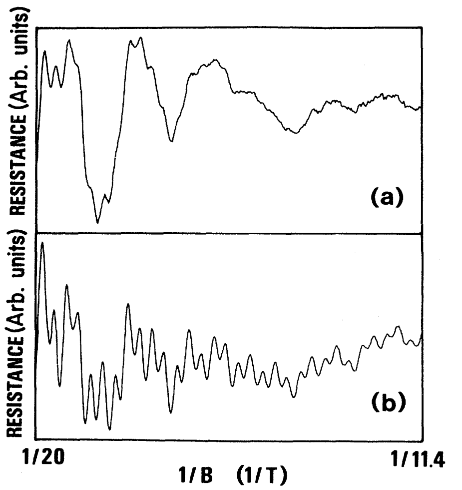

FIG. 1. Oscillatory part of the magnetoresistance for $K_{0.33}(H_2O)_{0.66}TaS_2$ at $T=4.2$ K (a) and $T=1.4$ K (b) as function of the inverse field.

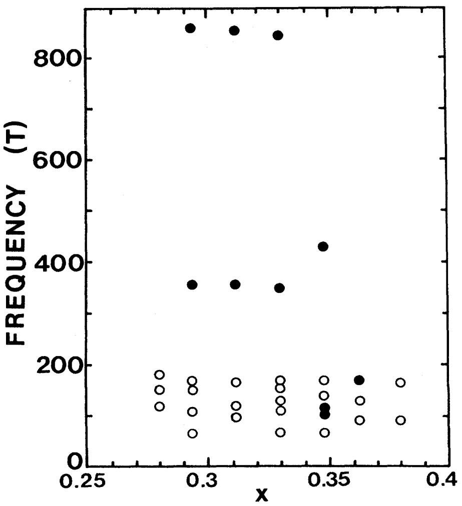

FIG. 3. Experimentally observed SdH frequencies as a function of the stoichiometry x in $K_x(H_2O)_yTaS_2$. Orbits with effective masses higher than 0.4 are represented by solid circles.

form of the data from Fig. 1(b) (for the extended field range $8 < B < 20$ T). The frequencies of the SdH oscillations which could be detected in our experiments are summarized in Fig. 3. [There is always some curvature of the nonoscillatory part of the magnetoresistance,[6] which gives rise to spurious low frequencies ($F < 50$ T) in the Fourier transform. These frequencies are not included in Fig. 3.]

For all stoichiometries x we find several oscillations below 180 T. In general, the amplitude of these oscillations varies only little with changing temperature, which signifies a low effective mass m/m_0 of the carriers (m_0 is the free-electron mass). The development of the frequencies with increasing charge transfer cannot be unambiguously followed in this regime. For $x=0.28$ we could detect no oscillations above 180 T, but for $x=0.295$ we find two frequencies at 355 and at 860 T which show a strong increase of amplitude upon lowering the temperature (high effective mass). These two higher frequencies are also observed for samples with $x=0.31$ and 0.33. The dependence on x is only weak. If the charge transfer is further increased ($x=0.347$) the higher frequencies become very small in amplitude, yet, we can unambiguously detect an oscillation at 430 T. Furthermore, we find at this stoichiometry two frequencies around 100 T with a high effective mass. For the sample with $x=0.362$ no frequencies higher than 180 T are detected, but there is one oscillation ($F=165$ T) with a strong increase in amplitude upon lowering the temperature. For the sample with $x=0.38$ we find a main broad peak in the Fourier spectrum ($F=165$ T) which represents very likely two frequencies close to each other.

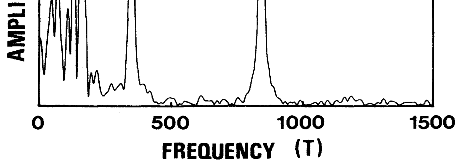

FIG. 2. Fourier transform for the data of Fig. 1(b) (field range 8 to 20 T).

The temperature dependence of the amplitude was used to calculate the effective cyclotron masses of the carriers. For the small orbits (frequency < 180 T) we find in general values between 0.05 and 0.2. But for $x=0.33$ there are two orbits with $m/m_0=0.3$, for $x=0.347$ there are two orbits at a frequency of about 100 T with $m/m_0=0.45$, and for $x=0.362$ the effective mass of the orbit with $F=165$ T is calculated to be 0.55. For the orbits corresponding to the two high frequencies which are detected for $x=0.295$ to $x=0.33$ we find $m/m_0=1.0$ (355 T) and $m/m_0=1.2$ (850 T).

The Dingle temperature T_D was determined only for the orbit with $F=845$ T ($x=0.33$). The analysis was done by plotting $\ln(A\sqrt{B})$ against $1/B$, with A being the amplitude of the oscillations and B the magnetic induction. This approximation is sufficiently accurate for our data. In this way, we find $T_D=3$ K. At 20 T the Landau-level separation ($h\omega_c$) is thus eight times as large as the broadening of the levels ($k_b T_D$).

For the samples with $x=0.295$ and 0.33 we also investigated the angular dependence of the two high-frequency oscillations. But, as is known from x-ray investigations, $2H$-TaS_2 prepared via the $1T$ form shows a large mosaic spread because of the phase transition from the $1T$ to $2H$ form. This mosaic spread is also present in the intercalation compounds and this is in our opinion the reason why we see oscillations only till ±22° from the perpendicular position. Within this range the angular dependence can be described by a cylindrical form of the Fermi surface (Fig. 4). An interesting feature is the occurrence of a spin-splitting zero at an angle of about 11° for the samples with $x=0.294$ and $x=0.33$ for the oscillations with $F=860$ T and $F=845$ T, respectively. (The absolute accuracy of the angle determination is only ±2°.) For this orientation alternative possible values of the spin-splitting factor g can be calculated: $g \sim 0.8, 2.5, 4.1$, etc.

Recently Guo and Liang[9] calculated the band structure of 2*H*-LiTaS$_2$ and showed that the rigid-band model (RBM) is essentially correct for this system. Since there are no band-structure calculations yet available for the hydrated metal intercalation compounds of 2*H*-TaS$_2$, we first apply a RBM to try to deduce the change of the Fermi surface by intercalation. According to the band-structure calculations of 2*H*-TaS$_2$ (Refs. 9–11) the Fermi energy lies in the middle of a half-filled *d* band well separated from the higher *d* bands. In contrast to results from early band-structure calculations,[10] it is now experimentally[12] and theoretically[9] clear that there is no gap between this low-lying *d* band and the sulfur *p* bands. The Fermi surface of 2*H*-TaS$_2$ consists of undulating holelike cylinders along the ΓA and KH lines of the hexagonal Brillouin zone.[11] The determination of the Fermi surface by Wexler and Woolley[11] shows that the average cross section of the cylinder along ΓA is slightly larger than those of the cylinders along KH. The undistorted 2*H*-TaS$_2$ should show oscillations in the range between 5500 and 9000 T. By intercalation, the dispersion along the c^* axis must be strongly reduced since the anisotropy in the resistivity increases by a factor of about 1000.[13] Since the Fermi surface is holelike, and we add electrons, the cylinders will shrink upon intercalation. In a linear approximation a charge transfer of 0.33 electrons per TaS$_2$ would yield a 33% reduction of the cross section. This means that the minimum frequency should still be higher than 3500 T. This is in contradiction with our experimental results, where we see only frequencies below 1000 T. It is very likely that we do not see all parts of the Fermi surface in our experiment; but the fact that several low-frequency oscillations are present is not in agreement with a simple RBM. In the following we will discuss several extensions of the RBM which could account for the experimental results.

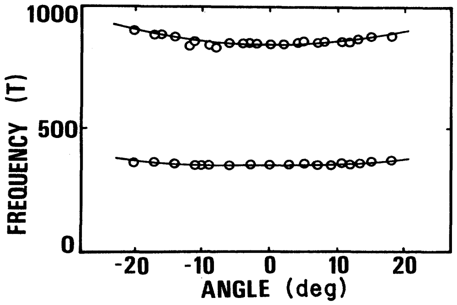

FIG. 4. Angular dependence of SdH frequencies for K$_{0.33}$(H$_2$O)$_{0.66}$TaS$_2$. The solid lines represent functions of the form $F(\theta=0)/\cos\theta$. θ is the angle between the crystal c axis and the magnetic field.

First we have to discuss the influence of the intercalate. The hydrated potassium ions can form a regular array in the interlayer space. For the compound with $x=0.33$ one would get a superstructure of $\sqrt{3}\times\sqrt{3}$ in the *ab* plane. This superlattice is commensurate with the original lattice. The new Fermi surface has to be calculated by folding back the bands into the new Brillouin zone. By this procedure pieces of the Fermi surface with small dimensions could appear. The fact that we see the high-frequency oscillations only for values of x near 0.33 supports an influence of the intercalate. But, as we have mentioned above, the samples are quench-cooled to avoid loss of the cointercalated water molecules. Ordering of the intercalate thus seems unlikely.

A second possible reason for the observed low frequencies could be the occurrence of a CDW. Wilson[14] has shown for 2*H*-TaSe$_2$ that a band folding according to the 3×3 superstructure due to the CDW, can give good agreement between band-structure calculations and experimental results (in these CDW phases of the 2*H* compounds a lot of low-frequency oscillations are detected[4,5] in contrast to the calculations for the undisturbed phase[10]). In the literature two possible observations of CDW in intercalation compounds are described: Scholz *et al.*[15] report observations of a CDW in electron diffraction patterns in Ag$_x$TaS$_2$ for $x<0.26$, and DiSalvo[16] shows some evidence from susceptibility measurements for a CDW in organic intercalation compounds of 2*H*-TaS$_2$. Resistivity measurements on K$_x$(H$_2$O)$_y$TaS$_2$ (Ref. 6) and TDPAC (time differential perturbed angular correlation) measurements[17] on the corresponding sodium compound, which has the same critical temperature of superconductivity, gave no hints for the presence of a CDW phase.

As a third possible explanation we mention the possibility of band shifting by intercalation. According to the latest band-structure calculations of 2*H*-TaS$_2$ (Ref. 9) the top of the sulfur *p* band is very near to the Fermi energy. If the intercalation process leads to an increased overlap of *d* and *p* bands there will also be *p*-electron bands at the Fermi energy. This speculative explanation is established by our experimental finding that there exist orbits with very different masses, which hints at the presence of two different bands. Earlier experimental work[6] on the temperature dependence of the resistivity (temperature $T<20$ K) has shown a T^3 dependence for K$_{0.33}$(H$_2$O)$_{0.66}$TaS$_2$. This can be explained by the existence of two bands with high and low mobility. The theoretical band-structure calculations of the intercalation compounds LiTiS$_2$ (Ref. 18) and LiTaS$_2$ (Ref. 9) have shown the occurrence of a shift. But in these compounds the Li intercalation yields an increase of the separation between the *d* and *p* bands.

Which of the above-mentioned models is correct cannot be decided at the moment. It is conceivable that a combination of the models is applicable. Band-structure calculations for these compounds would be of great interest.

In conclusion we have presented data showing the first observation of SdH oscillations in intercalation compounds of 2*H*-TaS_2. These oscillations cannot be explained in a simple rigid-band model. One has to take into account other effects like influence of overstructure, CDW effects, or band shifting by intercalation.

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