Superconductivity in $TaSi_2$ single crystals

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We have measured the magnetization and the specific heat of single-crystalline $TaSi_2$ at very low temperatures ($0.1\ K \le T \le 7.5\ K$). $TaSi_2$ is superconducting below $T_c \approx 0.353$ K, with $H_c(T=0\ K) \approx 2.98$ mT. We estimate and discuss the microscopic superconductivity parameters. $TaSi_2$ is found to be a type-I superconductor with weak electron-phonon coupling.

Among the silicides of transition metals, some of the $A15$ compounds, like V_3Si and Nb_3Si,[1] are known to be superconductors with high transition temperatures ($T_c = 17.1$ K for V_3Si). For the transition metal disilicides, however, superconductivity has only been reported for one compound, $CoSi_2$, with a critical temperature near 1 K.[2] Superconductivity has already been found in thin films of $TaSi_2$ and $NbSi_2$,[3] but has not been confirmed on bulk samples. In order to continue our previous investigations on the intrinsic characteristics and properties of the disilicides of transition metals,[4] we have measured the magnetization and the low temperature specific heat of $TaSi_2$ single crystals. $TaSi_2$ crystallizes in the hexagonal $C40$ structure (space group $P6_222$). Large single crystals of $TaSi_2$ were grown by a modified Czochralski technique.[5] These crystals were of large size (several cm^3), and of very good quality, which is reflected by the high residual resistance ratios (RRR > 400, see Refs. 4, 6, and 7). The largest crystal was used for specific heat measurements. Smaller samples for resistivity and magnetization measurements were cut from another crystal.

Magnetization measurements were made by the extraction (between two pick-up coils) technique; the field is given by a copper coil cooled by liquid nitrogen, and it can vary between -300 mT and $+300$ mT with small hysteresis. The low temperatures were obtained with a miniaturized dilution refrigerator,[8] which is moved with the sample. The sample was a single crystalline parallelepiped ($\approx 8 \times 0.6 \times 0.5\ mm^3$) with length along the $[10\bar{1}0]$ direction, mounted parallel to the field. In Fig. 1 we present the magnetization for two temperatures versus the effective magnetic field H_{eff} at the sample surface. We obtained H_{eff} by correcting the applied field with the demagnetization factor N. $N = 1.03 \times 10^{-2}$ had been determined from the sample shape and it corre-

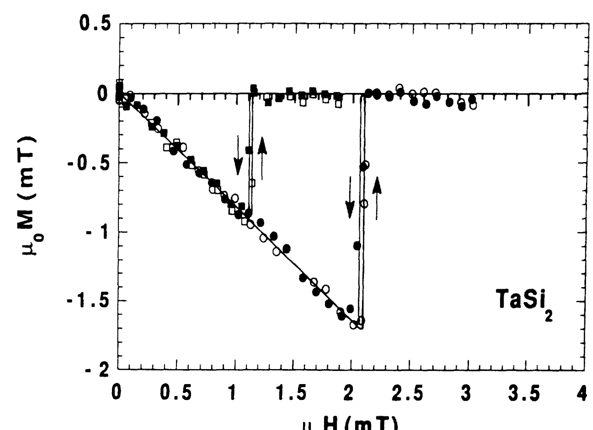

FIG. 1. Magnetization vs effective magnetic field for 0.1 K (○: increasing field; ●: decreasing field) and 0.25 K (□: increasing field; ■: decreasing field); plotted lines are a guide for the eye.

sponds to the value obtained from the transition width of our measurements before field correction. The magnetization increases linearly with the corrected field and then falls off sharply at the critical field H_c. The proportionality factor deviates only by about 8% from -1, which corresponds to 100% of diamagnetic shielding. This perfect diamagnetism is in favor of a 100% superconductivity in $TaSi_2$, which remains to be confirmed by specific heat measurements. The unique critical field and the absence of magnetic hysteresis are characteristics of type-I superconductivity. From interpolation of our results we estimate a transition temperature at zero field of about (345±10) mK and a critical magnetic field at zero temperature $H_c(0)=(2.6\pm0.3)$ mT for this particular sample.

The specific heat of another piece of single crystal (2.426 gr in weight) has been measured between 0.1 and 7.5 K on a dilution refrigerator. We used a transient heat pulse technique with a similar sample arrangement as already described.[9] A detailed analysis of the total specific heat will be given in a future paper. We only give here a short discussion of the electronic contribution to the specific heat C_e, and of the superconducting transition.

Above 1 K, $TaSi_2$ behaves like a normal metal with a specific heat that follows a $\gamma T+\beta T^3$ law. The value of β determined from a least-squares fit to the data in this temperature region is $\beta=0.058$ mJ/mol K^4, corresponding to a Debye temperature Θ of 465 K. This value is in good agreement with the Debye temperature determined from resistivity measurements.[6] At very low temperatures ($T<0.3$ K) we observe a specific heat increasing with decreasing temperature. This is due to the nuclear electric quadrupolar contribution, originating from the ^{181}Ta nuclei.[10] It follows a αT^{-2} law ($\alpha=0.136$ mJ K/mol). In Fig. 2 we represent the electronic contribution to the specific heat between 0.1 and 0.6 K. We obtained it after subtracting the phonon contribution βT^3 and the nuclear quadrupolar contribution αT^{-2} from the measured specific heat. We obtain a superconducting transition at $T_c=(353\pm3)$ mK. The transition temperature obtained by specific heat is in good agreement with that obtained from magnetization measurements. We note the very sharp transition width of about 6 mK.

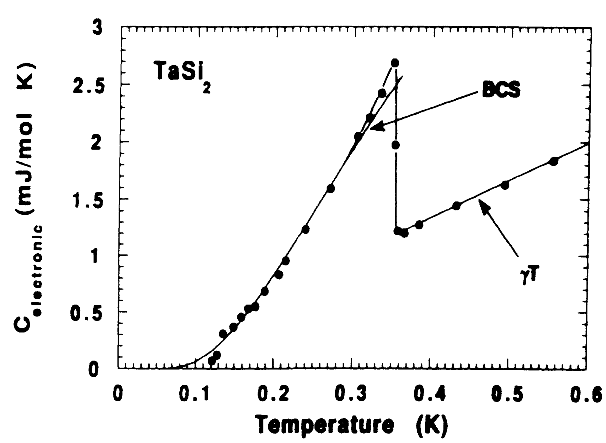

FIG. 2. Electronic part of the specific heat vs temperature compared to the exponential form given by BCS theory and compared with γT in the normal state.

Above the transition temperature, i.e., in the normal state, the electronic specific heat C_{en} increases linearly with temperature: $C_{en}=\gamma T$ with $\gamma=3.2$ mJ/mol K^2 just above T_c. Below the transition temperature the electronic part of the specific heat in the superconducting state C_{es}, vanishes exponentially. In Fig. 2 we have also plotted the exponential variation of the specific heat given by BCS theory:[11] $C_{es}/\gamma T_c=9.35\ \exp(-1.44T_c/T)$. Our data fit it very well if we take into account the important dispersion of our results, since the electronic part of the specific heat contributes by less than 10% to the total in this temperature range. The low temperature uncertainty is due to the large value of the subtracted nuclear term. The factor 9.35, which is determined by fitting, is very close to the BCS value of 8.5. Close to T_c, deviations from the exponential form are expected, since the exponential law is only valid for $T_c/T\gtrsim1.5$, i.e., $T\lesssim250$ mK. Close to the transition, the BCS model predicts a steeper rise of C_{es}. With our measurements, we obtain, for the jump at T_c in the specific heat,

$$\frac{\Delta C}{\gamma T_c}=1.40\pm0.05\ ,$$

where ΔC is the difference between the specific heat in the superconducting and the normal state at the transition temperature. This value is in very good agreement with the value of 1.43 given by BCS theory. Within a free electron model we can calculate the carrier density n from γ:

$$\gamma=\frac{\pi^2 k_B^2 N_0 m}{\hbar^2(3\pi^2 n)^{2/3}}\ .$$

N_0 is the Avogadro number and we have $n\simeq0.5\times10^{22}$ cm^{-3}, which is in very good agreement with the carrier density deduced from magnetoresistance measurements.[6]

From the Debye temperature Θ and the transition temperature T_c we have calculated the electron-phonon coupling parameter λ using the McMillan formula:[12]

$$T_c=\frac{\Theta}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right],$$

where μ^* is the Coulomb pseudopotential. If we use $\mu^*=0.1$, we obtain $\lambda=0.32$. We have also calculated the electron-phonon coupling parameter λ_{tr} from transport properties. In the high temperature limit, where the resistivity ρ is linear with T, it can be written as[13]

$$\rho=\frac{2\pi m k_B T}{ne^2\hbar}\lambda_{tr}\quad(T\gg\Theta)\ . \qquad (1)$$

The Bloch-Grüneisen formula gives, for ρ,[6]

$$\rho=A\left[\frac{T}{\Theta}\right]^5\int_0^{(\Theta/T)}\frac{z^5}{(e^z-1)(1-e^{-z})}dz$$

and, in the high temperature limit,

$$\rho=\frac{A}{4\Theta}T\quad(T\gg\Theta)\ . \qquad (2)$$

Relating Eqs. (1) and (2) we can calculate λ_{tr}. We use $A/\Theta \approx 0.5$ $\mu\Omega$ cm/K by taking the average for the three main crystallographic directions.[6] With $n \approx 0.5 \times 10^{22}$ cm^{-3}, we obtain $\lambda_{tr}=0.23$. Taking account of the very crude approximations, this result is in very good agreement with λ deduced from the McMillan formula. The small λ indicates that $TaSi_2$ is a superconductor in the weak-coupling limit, and so it should follow very well the BCS model.

The electron-phonon coupling causes γ to be enhanced by a factor $(1+\lambda)$ and we have

$$\gamma=(1+\lambda)\tfrac{1}{3}\pi^2 k_B^2 N(E_F) .$$

We take $\lambda=0.32$ and obtain, for the bare density of states, $N(E_F) \approx 1.0$ states/unit cell eV (three $TaSi_2$ by unit cell) and a charge carrier density $n \approx 0.7 \times 10^{22}$ cm^{-3}. The order of magnitude of n is not changed by the corrections. Using this value and in the framework of the free electron model we can calculate the microscopic superconducting parameters[14] (in SI units):

The coherence length ξ_0,

$$\xi_0=0.18\frac{\hbar v_F}{k_B T_c}=2.5\times 10^{-6}\text{ m} ,$$

the London penetration depth λ_L,

$$\lambda_L=\left[\frac{m}{\mu_0 n e^2}\right]^{1/2}=6.3\times 10^{-8}\text{ m} ,$$

and the parameter κ,

$$\kappa=\frac{\lambda_L}{\xi_0}=0.025 .$$

The small value of κ, i.e., $\xi_0 \gg \lambda_L$, confirms our result from the magnetization measurements, that $TaSi_2$ is a type-I superconductor. With the resistivity results from Ref. 6 we estimate the mean free path $l \approx 10^{-5}$ m. We have $l > \xi_0$, i.e., for our sample we find, that $TaSi_2$ is a superconductor in the "clean limit." Surely the free electron model is only a very crude approximation for the real material, but it indicates at least the orders of magnitude of the calculated values.

From the specific heat data in the superconducting state, we have calculated the critical field H_c as a function of temperature.[15] At $T=0$ K we have $H_c(0) \approx (2.98 \pm 0.1)$ mT, which is in quite good agreement with the result obtained by magnetization measurements. The slightly different values are not very surprising, since we used two samples cut off from different crystals. As usual, we have calculated $\gamma T_c^2 / V H_c^2(0) \approx 0.17$ (in cgs units, V is the molar volume), which correspond very well with the BCS limit of 0.168.[14] Finally, in order to show the good agreement of our results for $H_c(T)$ with BCS

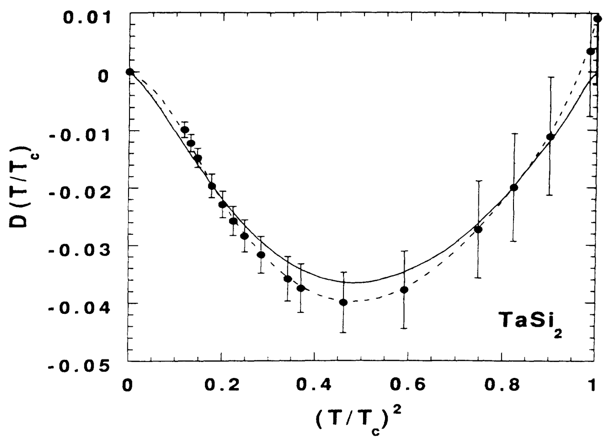

FIG. 3. $D=H_c(T/T_c)/H_c(0)-[1-(T/T_c)^2]$ vs $(T/T_c)^2$ (dashed curve) compared with BCS theory (full curve).

theory, we have plotted in Fig. 3 the deviation function $D(T/T_c)$ compared with BCS theory. $D(T/T_c)$ is defined by

$$D(T/T_c)=\frac{H_c(T/T_c)}{H_c(0)}-\left[1-\left[\frac{T}{T_c}\right]^2\right] ,$$

i.e., it describes the deviation of $H_c(T)$ from a parabola. The bars in Fig. 3 are an estimation of the uncertainty of our results.

Because of the long mean free path l, $TaSi_2$ is a superconductor in the clean limit. Like the majority of pure metals, it is a type-I superconductor. For $CoSi_2$, the transition temperature depends strongly on stoichiometry and on crystal defects.[2] Our samples of $TaSi_2$, however, are very pure with only few defects. This is confirmed both by the high residual resistance ratios[4,6,7] and by our results for two different samples, reported here, since they are the same in the limit of the precision of our different measurements. Nevertheless, crystal defects can strongly modify the superconducting properties, as it is suggested by the results from thin film measurements.[3] A detailed study must still be carried out before one can understand the influence of crystal defects and stoichiometry on the superconductivity of $TaSi_2$.

After $CoSi_2$, $TaSi_2$ is only the second transition-metal disilicide for which superconductivity has been found on bulk samples. By magnetization and specific heat measurements on different samples, we found a transition temperature of (0.353±0.003) K and a critical magnetic field at zero temperature of (2.98±0.1) mT. $TaSi_2$ is a type-I superconductor with weak electron-phonon coupling and its properties follow very well predictions of the BCS model.

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