Shubnikov–de Haas oscillations in $CoSb_3$ single crystals

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Shubnikov–de Haas (SdH) effect has been studied in single-crystal samples of p-$CoSb_3$ in pulsed magnetic fields up to 35 T. From the temperature dependence of the amplitude of the SdH oscillations the values of cyclotron effective mass were determined. It was found that the effective mass increases from $0.07m_0$ to $0.15m_0$ with increasing of the hole concentration, taking part in the SdH effect, from 0.46 to 4.06 $\times 10^{18}\,cm^{-3}$, indicating a nonparabolicity of the valence band of $CoSb_3$. The fundamental band parameters, the band-edge effective mass ($m_n^*/m_0 = 0.049 \pm 0.006$), energy gap ($E_g = 31 \pm 5$ meV), spin-orbit splitting ($\Delta = 0.16 \pm 0.06$ eV), and the interband momentum matrix element [$P = (2.0 \pm 2) \times 10^{-8}$ eV cm] were estimated using the three-band Kane model.

INTRODUCTION

$CoSb_3$ has recently been identified as a strong candidate for advanced thermoelectric materials.[1–4] Transport phenomena measurements were carried out on p-$CoSb_3$ single crystals, the temperature dependencies of the Hall coefficient, conductivity and Hall mobility were determined.[1–6] Data on the scattering mechanisms were reported.[2–4,6] Band-structure calculations from the first principles performed by Singh and Pickett[7] indicate the proximity of the linear-dispersing region to the band edge. The latter makes the skutterudite antimonides unique. It was also found that in $CoSb_3$ a pseudogap forms around the Fermi level, and that a single band crosses the pseudogap and forms a direct 50-meV gap at the Γ point.

The energy gap E_g and effective mass m^*/m_0 are the main band parameters, which determine the principal properties of any semiconducting material. However, there is little data on E_g and m^*/m_0 and the results obtained are not in conformity with one another. The estimated values of the hole density of states effective mass differs by a factor 5 (0.05[4] and 0.01[3] at the same hole concentration of about $6 \times 10^{16}\,cm^{-3}$) because of the different assumption about the predominant scattering mechanism in $CoSb_3$. The data available on the scattering mechanism are few and the results obtained are inconsistent.[2–4,6] Acoustic phonons scattering,[2,4] optical phonons scattering,[6] or ionized impurities scattering[3] have been assumed as dominant in $CoSb_3$.

The available values for the energy gap E_g are in the range of 0.05–0.7 eV [50 meV,[3,4,7] 0.31 eV,[3] 0.35 eV,[8] 0.5 eV,[9] and 0.6–0.7 eV (Ref. 5)]. The gap was estimated on the base of the band structure calculations,[7] low-[3] and high-temperature electrical resistivity measurements.[3,5,8,9] Optical measurements on a crystal grown by vapor phase showed no evidence of a semiconducting energy gap of any kind.[10]

The Shubnikov–de Haas (SdH) effect has proved to be an important tool of studying the band structure of semiconductors.[11] Recently, SdH oscillations measurements on $CoSb_3$ crystals were observed for the first time.[12] The values of cyclotron effective masse ($m^*/m_0 = 0.07 \pm 0.01$) and g factor (-10.1) were estimated for lightly doped $CoSb_3$ ($4.6 \times 10^{17}\,cm^{-3}$). It is also shown that in $CoSb_3$ the number of the equivalent valleys is equal to one and the Fermi surface of holes is likely to be a sphere located at the center of the Brillouin zone.

The purpose of our work was to learn more information about the band structure of $CoSb_3$ by extending the investigation of the SdH effect over a larger region of hole concentration (i.e., by going inside the band), to find effective mass values of holes as a function of the hole concentration, and to determine the fundamental band parameters, the energy gap E_g and interband momentum matrix element P. The determination of band parameters is more reliable when the hole concentration in the studied samples covers a wide range. Therefore, the results of SdH effect measurements on samples with 0.46 to $4.06 \times 10^{18}\,cm^{-3}$ are used.

Single crystals of $CoSb_3$ were grown from Sb-rich melts by the gradient freeze technique.[13] Co (4N) and Sb (6N) ampoules were prepared with a nominal composition of 93% at. Sb. A two-zone furnace was used. The growth process was carried out by lowering the temperature of the furnace. Studied p-type samples of nominally undoped $CoSb_3$ crystals were cut from an ingot. A gradient of carrier concentration was observed along the ingot which can be attributed to the existence of vacancies on the Co site. The concentration varies with the crystallization temperature. At 15–20 K, the Hall concentration ranges from 2 to $6 \times 10^{18}\,cm^{-3}$ and the mobil-

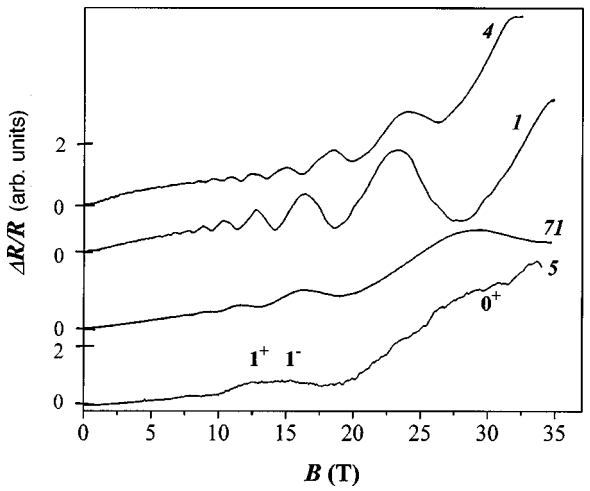

FIG. 1. Shubnikov–de Haas oscillations of samples 71ob22, 10ob19, 4ob17, and CS5 (curves 71, 10, 4, and 5, respectively). The latter is taken from Ref. 12.

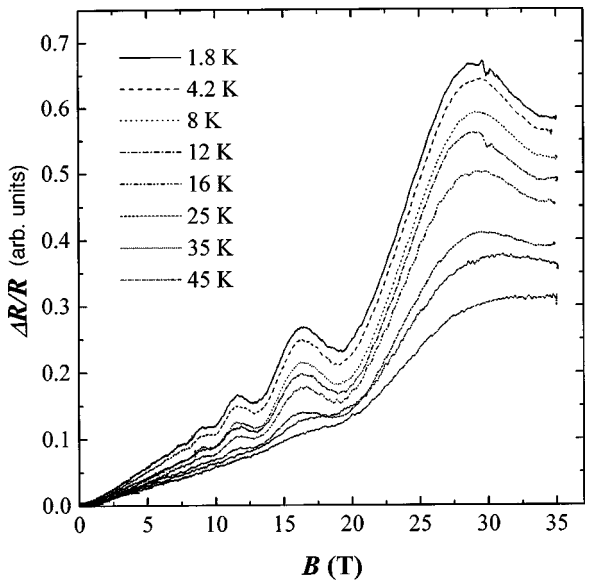

FIG. 2. Shubnikov–de Haas oscillations of sample 71ob22 at different temperatures.

ity varies between 1900 and 2400 cm^2/Vs.

The SdH measurements were carried out at different temperatures between 1.8 to 45 K in pulsed magnetic fields up to 35 T. The characteristics of the pulsed fields are detailed in Ref. 12. The magnetoresistance was measured during the decrease of the field, using a four probe techniques and Lockin amplifier.

RESULTS AND DISCUSSIONS

For the samples under study the three inequalities, namely, $E_F \gg k_B T$, $\hbar\omega \gg k_B T$, $\mu B \gg 1$ where E_F is the Fermi energy, ω is the cyclotron frequency, and μ is the mobility of the charge carriers which must be satisfied to observe the SdH effect were verified

SdH oscillations at 4.2 K in the unoriented $CoSb_3$ single crystals with concentration from 0.46 to $4.06\times10^{18}\,cm^{-3}$ in transverse configuration are shown in Fig. 1. Oscillations were observed up to 45 K (Fig. 2). All the samples studied show only one oscillation period. Splitting due to spin, which was earlier reported for lightly doped samples ($0.46\times10^{18}\,cm^{-3}$)[12] was not observed in samples with higher hole concentration (from 1.45 to $4.06\times10^{18}\,cm^{-3}$) in magnetic fields up to 35 T (Fig. 1). The transverse and longitudinal magnetiresistance show the same oscillation period which lead us to conclude that the hole Fermi surface is isotropic.[12]

If only the first harmonics describing the oscillatory components $\Delta\rho_1/\rho_0$ and $\Delta\rho_2/\rho_0$ are included, the oscillation term of the magnetoresistance may be written in the form,[14]

$$\frac{\Delta\rho}{\rho_0}=\frac{\Delta\rho_1}{\rho_0}+\frac{\Delta\rho_2}{\rho_0}, \tag{1}$$

$$\frac{\Delta\rho_1}{\rho_0}=-\frac{5}{\sqrt{2}}\left(\frac{\hbar\omega}{\eta}\right)^{1/2}\frac{x}{\sinh x}\exp(-y)\cos\left(\frac{2\pi\eta}{\hbar\omega}-\frac{\pi}{4}\right), \tag{2}$$

$$\frac{\Delta\rho_2}{\rho_0}=-\frac{3\pi\hbar\omega}{8\eta}\frac{x}{\sinh x}\exp(-y)\cos\left(\frac{2\pi\eta}{\hbar\omega}-\frac{\pi}{2}\right), \tag{3}$$

with $x=14.68Tm^*/m_0B^{-1}$, $y=14.68T_{D(\mathrm{SdH})}m^*/m_0B^{-1}$, $\omega=eB/m^*$, and $\eta=E_F/k_BT$ is the reduced Fermi energy, m^* is the hole effective mass, m_0 is the free hole mass, $T_{D(\mathrm{SdH})}$ is the Dingle temperature determined from the SdH oscillations.

It can be shown that[15]

$$\frac{\Delta\rho_1}{\Delta\rho_2}=\frac{20}{3\pi}\left[\frac{1}{\Delta(1/B)B}\right]^{1/2}\left\{1+\mathrm{cotan}\left[\frac{2\pi}{\Delta(1/B)B}\right]\right\}, \tag{4}$$

where $\Delta(1/B)$ is the period of oscillations.

Taking into account that in the samples studied ($\Delta\rho_1/\Delta\rho_2 \gg 1$), the value of $T_{D(\mathrm{SdH})}$ was calculated using Eq. (2) from the magnetic field dependence of the oscillation amplitude. $T_{D(\mathrm{SdH})}$ are greater than the values of $T_{D(\mu)}$ determined from the Hall mobility[11] $T_{D(\mu)}=\hbar e/2\pi k_B m^*\mu$ which indicated that the nonthermal broadening of the levels

TABLE I. Parameters of the samples.

Sample	p_{SdH} ($10^{18}\,cm^{-3}$)	m^*/m_0	$T_{D(\mathrm{SdH})}$ (K)	$T_{D(\mu)}$ (K)	E_F (meV)	η (at 15 K)
CS5*	0.46	0.07	20	1.4	33.5	25.8
71ob22	1.45	0.11	19	8.2	41.9	32.3
1ob19	2.31	0.13	15	8.7	50.9	39.3
4ob17	4.06	0.15	12	7.7	64.4	49.7

*Data are taken from Ref. 12.

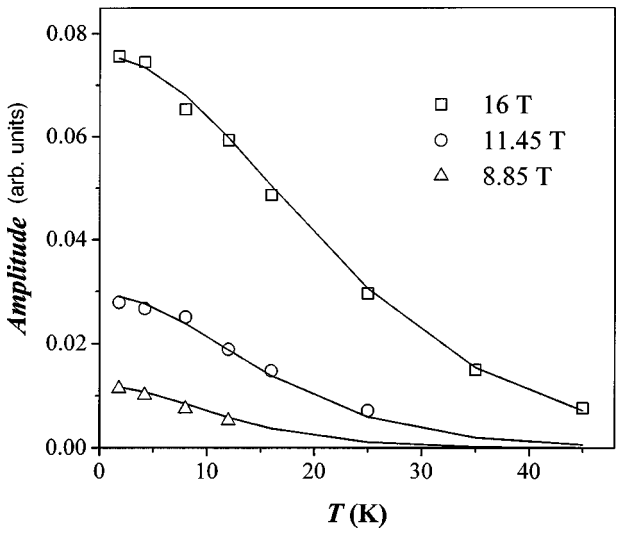

FIG. 3. The temperature dependencies of the oscillation amplitude of sample 71ob22.

was mainly due to the inhomogeneity of the samples rather than to the scattering of holes (Table I).

The concentration p_{SdH} of the holes participating in the SdH effect was evaluated using Eq. (5) (Ref. 14) from the periodicity of the SdH oscillations

$$p_{\mathrm{SdH}}=\left(\frac{2e}{\hbar}\right)^{3/2}\frac{[\Delta(1/B)]^{-3/2}}{3\pi^2}, \tag{5}$$

where $\Delta(1/B)$ is the period of the oscillations.

The values of the cyclotron effective masse m^*/m_0 were determined by an analysis of the temperature dependencies of the oscillation amplitude in the temperature range 1.8–45 K at fixed magnetic field (Fig. 3) and were used in the calculation of $T_{D(\mathrm{SdH})}$. The effective mass increases from $0.07m_0$ to $0.15m_0$ with increasing hole concentration taking part in the SdH effect, from 0.46 to $4.06\times10^{18}\,\mathrm{cm}^{-3}$ (see Table I), indicating a nonparabolicity of the valence band of $CoSb_3$ which has not been established yet.

Kane showed that, due to the narrow energy gap between the conduction and the valence bands, the energy wave-vector dependences in the conduction and light-hole bands differ appreciably from the simplest parabolic relation.[16] Since the nonparabolic shape of the conduction band in InSb had been derived by Kane, it was recognized that the band nonparabolicity must be taken into account when interpreting the electron transport phenomena in narrow gap materials.[17]

Singh and Pickett[7] predict that in $CoSb_3$ the dispersion, although parabolic in a very small region (10^{-5} of the zone) near Γ point, rapidly becomes linear in energy at small wave vectors. However, it is not yet proved experimentally. That is why the Kane model, used for other narrow gap semiconductors, can be used to describe the results obtained. The analysis were performed on the basis of the two- and three-band Kane model.

The Fermi surface of holes in $CoSb_3$ is likely to be a sphere located at the center of the Brillouin zone.[12] Therefore the concentration p of the holes participating in the Hall effect should be equal to the concentration p_{SdH} of the holes participating in the SdH effect. The concentration p of the holes could be determined on the base of the equation,[18]

$$p=\frac{(2m_nk_BT)^{3/2}}{3\pi^2\hbar^3}\frac{\left(1+\frac{2\delta}{3}\right)^{3/2}}{(1+\delta)^{3/2}}I^0_{3/2,0}(\eta,\beta,\delta), \tag{6}$$

where m_n is the band-edge effective mass, $I^0_{3/2,0}$ is the three parameters Fermi-Dirac integral, $\beta=k_BT/E_g$, $\delta=\Delta/E_g$, Δ is the spin-orbit splitting value. In the strongly degenerate case ($\eta\geqslant10$), $I^0_{3/2,0}(\eta,\beta,\delta)$ can be evaluated as arithmetic expression in terms of the three variables.[18,19]

Equation (6) can be written as

$$\frac{p_l}{p_k}=\frac{I^0_{3/2,0}(\eta_1,\beta,\delta)}{I^0_{3/2,0}(\eta_k,\beta,\delta)}, \tag{7}$$

where p_l is the hole concentration for sample l, η_k is the reduced Fermi level for sample k.

The reduced Fermi level was calculated from Eq. (8),

$$\eta=\left(n+\frac{1}{2}\right)\frac{\hbar\omega}{k_BT} \tag{8}$$

where n is the Landau numbers. For samples studied $E_F>30\,\mathrm{meV}$ and $\eta>10$ at low temperatures (see Table I).

The value of $\beta=k_BT/E_g$ was estimated using Eqs. (7) and (8). It was found that at low temperatures $Eg=35\pm2$ meV if $\delta\ll1$ or $\delta\gg1$ (two-band Kane model approximation) and $Eg=31\pm5$ meV if three-band Kane model is assumed. The values of m_n/m_0 estimated using Eqs. (6) and (8) are equal to 0.050 ± 0.002 or 0.049 ± 0.006, respectively if two- or three-band Kane model is assumed.

To estimate the value of Δ and the interband momentum matrix elements P and E_p, the data on g factor, determined on the base of the SdH oscillations measurements on lightly doped $CoSb_3$ crystals from the spin-splitting SdH peak,[12] were used. In the framework of a nonparabolic three band Kane model the values of g factor, $m^*/m_0, m_n^*/m_0$ and the interband momentum matrix elements E_p and P are given by[18]

$$g(E)=2\left[1+\left(1-\frac{m_0}{m_n^*}\right)\frac{\Delta}{(3E+3E_g+2\Delta)}\right], \tag{9}$$

$$\frac{m^*}{m_0}=\frac{1}{E_p}\frac{\lfloor(2E+E_g)(E+E_g+\Delta)(E+E_g+2\Delta/3)-E(E+E_g)\Delta/3\rfloor}{(E_g+\Delta)E_g(E+E_g+2\Delta/3)^2}, \tag{10}$$

$$\frac{m_n^*}{m_0}=\frac{E_g(E_g+\Delta)}{E_p(E_g+2\Delta/3)}, \tag{11}$$

$$E_p=\frac{2m_0P^2}{\hbar^2}. \tag{12}$$

The values of Δ, E_p, and P were calculated using Eqs. (9)–(12), respectively, with $E_g=31\pm5$ meV and $m_n^*/m_0=0.049\pm0.006$ in accordance with our estimation and $g(E)=-10.1$ for lightly doped sample ($p=4.6\times10^{17}\,\mathrm{cm}^{-3}$, $E=0.0335$ eV).[12] It was found that $\Delta=0.16\pm0.06$ eV, $P=(2.0\pm2)\times10^{-8}$ eV cm and $E_p=1.1\pm0.2$ eV.[20]

The obtained value of m_n^*/m_0 is lower than that earlier reported ($m_n^*/m_0=0.071$)[4] and much lower than that of m^*/m_0 indicating the strong nonparabolicity of the valence band of $CoSb_3$.

Our data on E_g confirm the theoretical prediction[7] that $CoSb_3$ is a semiconductor with a very narrow gap. The estimated value of E_g (31 ± 5 meV) is lower than the theoretical predicted value (50 meV) (Ref. 7) and also lower than recent experimental estimates of 50 meV.[3,4] The value of P is in satisfactory agreement with those reported for III-V and II-VI compounds.[21,22]

In the framework of the Kane model the effective mass is expressed as[18,23]

$$\left(\frac{\dfrac{m^*}{m_0}}{1-\dfrac{m^*}{m_0}}\right)^2=\left(\frac{m_n}{m_0}\right)^2+\left(\frac{m_n}{m_0}\right)^2\frac{2\hbar^2(3\pi^2)^{2/3}p^{2/3}}{m_nE_g} \tag{13}$$

if $\Delta\gg E_g$ and $(E-\hbar^2k^2/2m_0)\ll E_g+2/3\,\Delta$ (where E is the energy of the hole), or

$$m^*=\hbar^2\left(\frac{3}{2P^2}\right)^{1/2}(3\pi^2)^{1/3}p^{1/3} \tag{14}$$

if $\Delta\gg E_g$ and $E_F\gg E_g$.

The dependencies $[m^*/m_0/1-(m^*/m_0)]^2$ upon $p^{2/3}$ and m^*/m_0 vs $p^{1/3}$ are linear, in agreement with Eqs. (13) and (14), respectively (Fig. 4), and prove the nonparabolicity of the valence band up to hole concentration of $4.06\times10^{18}\,\mathrm{cm}^{-3}$. The latter dependence is in agreement with the Singh and Pickett model too.[7] They predict that, in $CoSb_3$, the dispersion, although parabolic in a very small region (10^{-5} of the zone) near the Γ point, rapidly becomes linear for moderate levels of hole doping as low as $3\times10^{16}\,\mathrm{cm}^{-3}$.

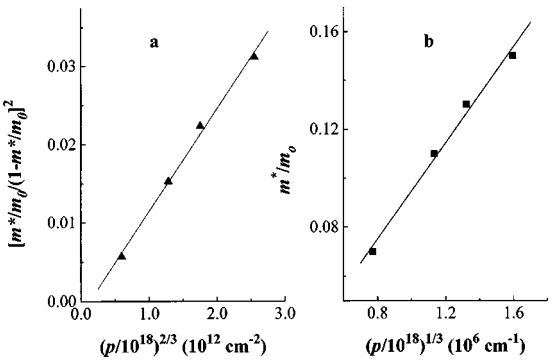

FIG. 4. (a) The dependence of $[m^*/m_0/1-(m^*/m_0)]^2$ upon $p^{2/3}$. (b) The dependence of m^*/m_0 vs $p^{1/3}$.

Therefore, the results obtained are in satisfactory agreement with both the Kane model and the Singh and Pickett band structure calculations.[7] To established the character of the nonparabolicity of the valence band in $CoSb_3$ (Kane or Singh and Pickett model[7]) study of lightly doped crystals (down to $3\times10^{16}\,\mathrm{cm}^{-3}$) are necessary.

SUMMARY

In summary, the results of Shubnikov–de Haas oscillations measurements on $CoSb_3$ crystals were used to obtain the values of the hole effective mass and its dependence on the hole concentration. It was found that the valence band in $CoSb_3$ is nonparabolic. The effective mass increases from $0.07\,m_0$ to $0.15\,m_0$ with increasing of hole concentration, taking part in the Shubnikov–de Haas effect, from 0.46 to $4.06\times10^{18}\,\mathrm{cm}^{-3}$. The fundamental band parameters, the band-edge effective mass, energy gap, spin-orbit splitting, and the interband momentum matrix element were estimated, using the three-band Kane model.

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