Electronic structure of cobalt disilicide

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The electronic structure of $CoSi_2$ at the Fermi level has been investigated by means of the de Haas–van Alphen effect in pure crystals. The measured Fermi-surface areas may be understood in terms of three bands crossing the Fermi level as predicted in a recent energy band calculation of Mattheiss and Hamann (following paper). The experimental and the predicted areas associated with all three bands are found to agree to a remarkable accuracy of better than 6%, while the measured cyclotron masses exceed the calculated masses by 40% to 100% for the smallest and the largest Fermi-surface sheets, respectively. The latter result points to a substantial and anisotropic suppression of the slopes of the quasiparticle bands at the Fermi level due to the electron-electron and electron-phonon interactions.

I. INTRODUCTION

Cobalt disilicide, a metal with a cubic (CaF_2) crystal structure having a lattice constant which is within 1% of that of pure silicon, has proved to be ideally suited for the formation of sharp and strain-free metal-semiconductor interfaces which are of theoretical and technological interest. For this reason, the properties of $CoSi_2$ and, in particular, of thin films grown epitaxially on silicon, have been the subjects of many recent investigations. As an example of a material which, though composed of a magnetic element (Co), becomes superconducting at low temperatures (below 1.5 K in pure samples[1]), $CoSi_2$ is also of interest in its own right in the field of magnetism and superconductivity.

The present work was carried out to help clarify the intrinsic properties of bulk samples of $CoSi_2$. In the following we outline a procedure used to prepare crystals of this system with a purity five times higher than that previously reported. These samples have been the basis of several investigations and here we present the results of measurements of the quantum oscillatory or the de Haas–van Alphen (dHvA) magnetization as a function of magnetic field intensity and orientation, and as a function of temperature. The Fermi-surface areas and cyclotron masses inferred from these measurements are used in conjunction with recent electronic structure calculations[2,3] to develop a realistic picture of the quasiparticle bands near the Fermi level, in a first step towards an understanding of the band structure of high-quality metal and semiconductor layers.

II. MATERIAL PREPARATION

Bulk $CoSi_2$, which is thought to be congruently melting at 1326 °C, is usually prepared by slow solidification from a stoichiometric melt. This procedure leads to excellent crystals but even when very pure melts are employed, the samples so produced exhibit surprisingly low values of the residual resistivity ratio $[\rho(300\ \mathrm{K})/\rho(4.2\ \mathrm{K})]$ of the order of 5 (Ref. 4 and this work). Analyses of some of these samples by a scanning electron microprobe show that the low values of the resistance ratio can be attributed to Co and Si segregation, which is much more extensive than conventional metallurgical phase diagrams would suggest.[5]

To reduce segregation a rapid cooling procedure which produced single crystals of suitable dimensions and quality has been employed. The starting materials, Co and Si, were obtained from Materials Research, Orangeburg, New Jersey, and from Metal Crystals, Cambridge, U.K., respectively. The high-purity Co had a residual resistance ratio of 135 and the Si had less than 1 ppm wt. total metallic impurities (but may have contained up to 90 ppm wt. of oxygen). One-gram charges of etched Co and Si were melted and annealed in a water-cooled copper boat under purified Ar using rf heating. As compound formation was accompanied by a high heat of reaction the silicon was added to the cobalt in four separate melts. The sample was remelted and rotated three times so that any solid layer in contact with the copper would be mixed in, being held molten over 30 min in all. It was then taken above the melting point, at which point the rf power was cut. This achieved a quench at 100 °C per second. Finally, it was annealed at 160 °C below the melting point for one day. The difference in mass between the constituents and the final ingot was less than 0.1%. The resistance ratio varied between 15 and 25 throughout the sample, i.e., a result reaching five times the level previously achieved. No inhomogeneities in composition in this sample could be detected by scanning electron microanalysis over the scales 500–1 μm (the limit of the machine). Laue x-ray analysis confirmed that the crystals in the sample are of high quality with a low mosaic spread (below the limit of detection of 0.2°). Two samples were spark-cut from the ingot. The first sample, which is polycrystalline and has a resistance ratio of 25, has been the basis of transport measurements which confirm a room-temperature (300 K) resistivity of 12.5 $\mu\Omega$ cm, a helium-temperature (4.2 K) resistivity of 0.5 $\mu\Omega$ cm and a superconducting transition temperature of

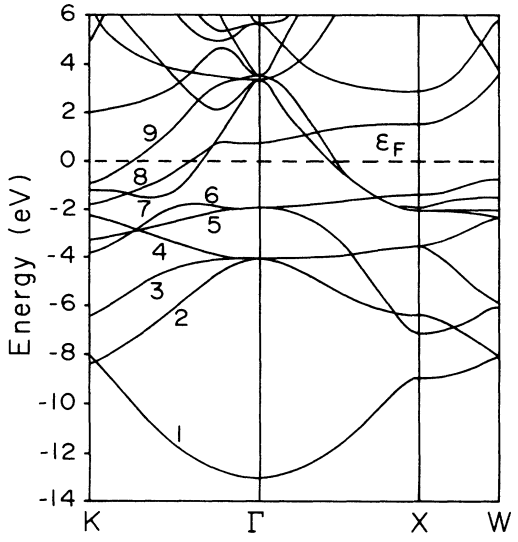

FIG. 1. The energy bands of $CoSi_2$ along principal symmetry directions calculated by Mattheiss and Hamann by means of the linear augmented-plane-wave method (Ref. 3). Bands 7, 8, and 9 cross the Fermi level and give rise to sheets 7, 8, and 9, respectively, of the Fermi surface in Fig. 2. The effect of the spin-orbit interaction, which is expected to lift many of the band degeneracies, is not included.

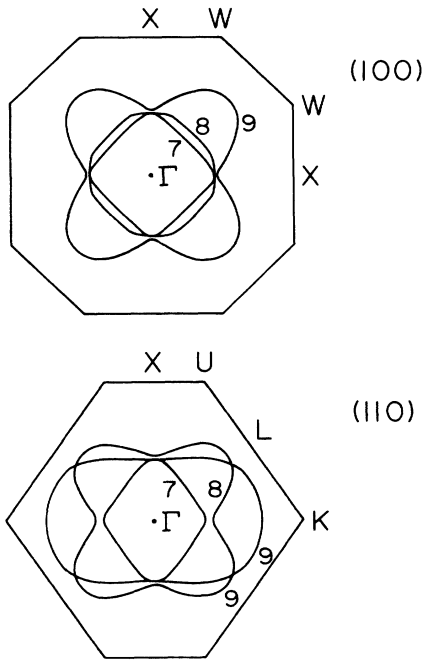

FIG. 2. Principal sections through the Fermi surface of $CoSi_2$ in the (100) and (110) planes for the band model described in the caption of Fig. 1. The Brillouin zone is that of the cubic CaF_2 crystal structure.

1.5 K.[1] The second sample, a $2\times1\times0.5$-mm^3 single crystal with a resistance ratio of 15, has been used in the present measurements of the dHvA magnetization (Secs. IV and V). Samples of much greater purity might be produced by the above method via straightforward improvements in the purity, degree of stoichiometry and homogeneity of the melt, the purity of the (flowing) argon gas, the rate of quenching of the melt, and the annealing procedure.

III. BAND STRUCTURE

Calculations of the electronic structure of $CoSi_2$ performed by Mattheiss and Hamann[3] using the linear augmented-plane-wave method suggest that three bands of s and p character cross the Fermi level to give rise to three concentric hole sheets centered on the Γ point of the fcc Brillouin zone. The calculated bands along some principal symmetry directions and the (100) and (110) central sections through the Fermi surface, which will be the basis of our discussions below, are presented in Figs. 1 and 2, respectively. The three sheets labeled 7, 8, and 9, respectively, give rise to the values of extremal areas, in

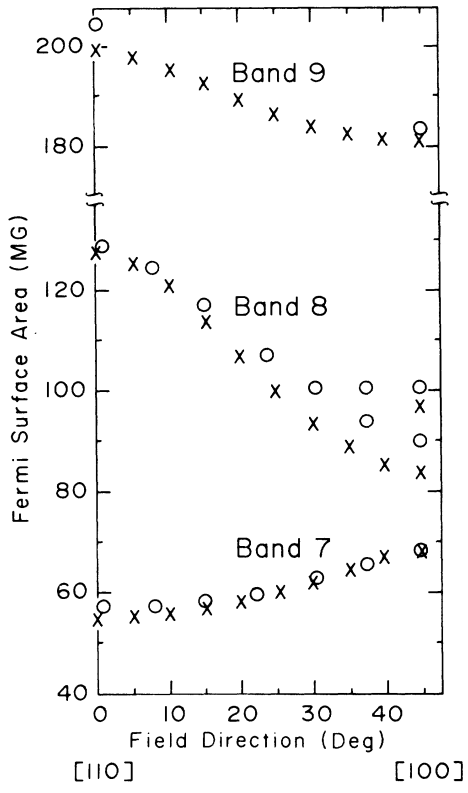

FIG. 3. Variation of the observed (○) and calculated (×) dHvA frequencies for field directions in the (001) plane. The lower, the intermediate, and the upper experimental branches are labeled α, β, and γ, respectively, in Table I. The corresponding calculated branches arise from bands 7, 8, and 9, respectively. The third branch from the bottom near [100] is attributed to a noncentral extremal area on sheet 8 and is labeled δ in Table I. The conversion of dHvA frequencies F (in MG) to extremal areas A (in Å^{-2}) is given by the factor 9.546×10^{-3} Å^{-2}/MG.

planes normal to the applied magnetic field, given by the crosses in Fig. 3, when the field is oriented in the (001) plane. All calculated areas are extremal and are in central planes, with the exception of the upper area associated with band 8 near [100] (which arises from a noncentral plane not shown in Fig. 2). The cyclotron masses associated with the central extremal areas in symmetry planes have also been calculated and the results will be discussed in Sec. V.

IV. MEASUREMENTS OF THE FERMI SURFACE AND CYCLOTRON MASSES

The applicability of the above band-structure model has been investigated by measurements of the dHvA magnetization $\tilde{M}$ which yields, from the frequencies F of the oscillations in the reciprocal of the magnetic induction B, the extremal areas of the Fermi surface

$$A = 2\pi eF/\hbar c \ ,$$

and, from the temperature dependence of the amplitude of the oscillations, the cyclotron mass

$$m^* = \frac{\hbar}{2\pi}\oint \frac{dk}{v_{\mathbf{k}}} = \frac{\hbar^2}{2\pi}\left[\frac{\partial A}{\partial \varepsilon}\right]_{\varepsilon_F} ,$$

where $v_{\mathbf{k}} = |\hat{\mathbf{B}}\times\nabla_{\mathbf{k}}\varepsilon|/\hbar$ is the appropriate component of the Fermi velocity and the integral is over the perimeter of A (on the cyclotron orbit).

The measurements of $\tilde{M}$ were performed using a 13-T superconducting magnet and a ^{3}He cryostat that could cool the sample to 0.35 K. The signal was detected using a field-modulation technique adjusting both the modulation amplitude and frequency to maximize the signal-to-noise ratio. Most measurements were taken modulating at 240 Hz and detecting on the fourth harmonic. The quasistatic magnetic field was calibrated using the known dHvA frequencies in an oriented gold crystal.[6] The dHvA frequencies were obtained from the Fourier spectra averaged over up and down magnetic field sweeps. (The Fourier spectrum here is the square root of the sum of the squares of the real and imaginary parts of the Fourier transform of the data multiplied by a cosine window and padded with zeroes to increase the density of points for accurate amplitude and frequency determinations.)

The cyclotron masses were determined along symmetry directions from the temperature dependence of the amplitudes of the oscillations as mentioned above. The temperature was measured via both a calibrated carbon resistor and the vapor pressure of ^{3}He. (More detailed discussions of the techniques employed may be found, for example, in Refs. 7 and 8.)

V. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

The measured values of the dHvA frequencies and cyclotron masses for a magnetic field applied along the [100] and [110] symmetry directions are given in Tables I and II, and the values of the measured frequencies for field directions in the (001) plane are given by the open circles in Fig. 3. The three fundamental frequencies labeled α, β, and γ may be identified from their magnitudes and (for the α and β branches) the orientation dependence, with central extremal areas of the Fermi surface calculated for bands 7, 8, and 9, respectively. The frequency branch labeled δ is consistent with the behavior expected for a noncentral extremal area associated with sheet 8. As shown in Table I, the measured and calculated areas agree to an accuracy of better than 6% in all cases. Since there are no adjustable parameters in the calculations this level of agreement is striking.

The measured cyclotron masses of the central extremal areas at [100] and [110] are also compared with the corresponding calculated band masses in Table I. All experimental masses are enhanced above the band masses by a significant amount varying from 40% for sheet 7 to 100% for the largest sheet 9. This indicates that the renormalization of the slopes of the quasiparticle bands at the Fermi level due to the electron-phonon and the electron-electron interaction is quite substantial and larger than normally expected for simple metals [it is comparable to

TABLE I. Summary of experimental and calculated dHvA frequencies and cyclotron masses for the [100] and [110] symmetry directions. The α, β, and γ branches are associated with the central extremal areas of sheets 7, 8, and 9, respectively. The δ branch is associated with a noncentral extremal area of sheet 8. The last column gives the mass renormalization factor.

			Frequencies (MG)		Cyclotron masses (m_e)		
Orientation	Branch	Orbit	Expt.[b]	Calc.	Expt.	Calc.	Expt./Calc.
[100]	α	7	68.6	67.8	0.78(1)	0.54	1.4
	β	8	89.8	84.3	1.36(10)	0.82	1.7
	γ	9	183.0	181.2	2.00(7)	1.28	1.6
	δ	8[a]	100.9	96.7	1.34(2)		
[110]	α	7	57.1	54.9	0.70(1)	0.51	1.4
	β	8	128.9	127.3	1.55(10)	1.06	1.5
	γ	9	204.1	199.0	2.47(10)	1.25	2.0

[a]Noncentral orbit.

[b]The uncertainties in the measured frequencies, principally due to small inaccuracies in the alignment of the magnetic field, are in all cases less than 1%.

TABLE II. dHvA frequencies intermediate between the frequencies F_α and F_β of the α and β branches in Table I. Near [100] three frequencies equally spaced $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the way between F_α and F_β, and near [110] one frequency $\frac{1}{2}$ of the way between F_α and F_β, are observed. These frequencies are consistent with the occurrence of magnetic breakdown at points of contact between sheets 7 and 8 along ΓX in Fig. 2. (The exact degeneracy may be lifted when the spin-orbit interaction is taken into account.) The measured values of these frequencies and masses agree within experimental error with the values of $F_\alpha+f(F_\beta-F_\alpha)$ and of $m_\alpha^*+f(m_\beta^*-m_\alpha^*)$, respectively, expected in terms of magnetic breakdown, where $f=\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$, and m_α^* and m_β^* are the measured cyclotron masses of the α and β branches, respectively, given in Table I.

		Frequencies (MG)		Cyclotron masses (m_e)	
Orientation	f	Experiment	$F_\alpha+f(F_\beta-F_\alpha)$	Experiment	$m_\alpha^*+f(m_\beta^*-m_\alpha^*)$
[100]	$\frac{1}{4}$	73.9(1)	73.9(1)	0.93(4)	0.93(4)
	$\frac{1}{2}$	79.2(1)	79.2(1)	1.05(10)	1.07(10)
	$\frac{3}{4}$	84.5(1)	84.5(1)	1.17(10)	1.22(10)
[110]	$\frac{1}{2}$	92.8(2)	93.0(2)	1.14(7)	1.13(10)

that recently reported, for example, in the incipient ferromagnet Ni_3Ga (Ref. 9)]. The magnitude and the anisotropy of the mass renormalization have not yet been accounted for theoretically.

We point out that, in addition to the fundamental frequencies discussed above, a number of components equally spaced between the α and β frequencies have also been observed (Table II). These find a natural interpretation if one takes account of magnetic breakdown, or the tunneling of carriers, between sheets 7 and 8, which nearly touch along the ΓX lines of the Brillouin zone. Magnetic breakdown is expected to lead to three intermediate branches, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the way between the α and β branches, when the magnetic field is along [100], and one branch halfway between the α and β branches when along [110], in agreement with experiment (Table II). This behavior (near [100]) is similar to that observed recently for certain sheets of the Fermi surface in the weakly magnetic metals Ni_3Al and Ni_3Ga,[9] and also in the heavy electron superconductor UPt_3.[10] We note that magnetic breakdown is also expected to arise between sheet 8 and sheet 9 (whose associated dHvA signal is very weak and only observable near the [100] and [110] symmetry directions (Fig. 3)). Signals associated with breakdown orbits on sheets 8 and 9 would be expected to be observed in samples of even higher purity than that used in the present work.

In conclusion, the measurements of the Fermi-surface areas and cyclotron masses, in conjunction with the electronic structure calculations of Mattheiss and Hamann, have helped elucidate the band structure of $CoSi_2$ at the Fermi level. All dHvA frequencies, including the intermediate (equally spaced) frequencies between the α and β branches, find a natural explanation in terms of the calculated band model and the measured and calculated extremal areas match to a surprising degree. The mass-renormalization factor is for all sheets larger than expected for a simple metal and we conclude that the slopes of the bands at the Fermi level are significantly modified, in a band-dependent way, by the dynamical part of the electron-phonon and electron-electron interactions. The precise mechanism for this renormalization remains to be worked out.

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