PHYSICAL REVIEW VOLUME 183, NUMBER 3 15 JULY 1969

Measurement of the de Haas–van Alphen Effect in the Pyrite-Type Structure SiP_2

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(Received 20 January 1969)

The de Haas–van Alphen effect was measured in an oriented single crystal of SiP_2 in magnetic fields up to 59 kG and temperatures down to 1.14°K. Several groups of oscillations were observed with frequencies ranging from 6.08×10^6 to 2.34×10^7 G and masses ranging from $0.13m_e$ to $0.33m_e$.

INTRODUCTION

THE new pyrite-type compound SiP_2 has recently been reported.[1] The SiP_2 was prepared by halogen transport of Si and P in a sealed silica tube. This compound was shown to be a metallic conductor, the room temperature resistivity being 3×10^{-5} Ω cm.[1] This feature is unusual since Si and P are normally semiconductors showing metallic behavior only in high-pressure forms.[2,3] A study of the de Haas–van Alphen effect was undertaken to elucidate this behavior.[4]

The pyrite-type crystal structure was verified for SiP_2 by x-ray powder diffraction.[1] The structure is cubic with point group symmetry $m3$ and space group $Pa3$. The unit cell contains four formula units. The silicon atoms are in the fourfold face-centered cubic position, while the P atoms are in the eightfold position xxx. The x parameter is 0.3922 ± 0.0005, which requires the P atoms to be paired at (2.13 ± 0.03) Å. The pairs of P atoms occupy positions in the center of the cell and along each edge. The resulting coordination of Si is trigonally-distorted octahedral, being surrounded by six P atoms. Each P is surrounded by a trigonally-distorted tetrahedron composed of three silicon atoms and the other half of the P pair.

de Haas–van Alphen Effect

The de Haas–van Alphen effect measures the oscillatory part of the diamagnetic susceptibility which is periodic in inverse magnetic field. The frequency of the oscillation F is equal to $\hbar cA/2\pi e$, where A is an extremal cross-sectional area of a sheet of the Fermi surface in k space in a plane perpendicular to the direction of the applied magnetic field H. The amplitude of the signal is a function of temperature and is proportional to

$$Te^{-2\pi^2 kcTm^*/\hbar eH},$$

where T is the temperature of the sample and m^* is the effective mass of the carriers giving rise to the signal.

Experimental Details

The SiP_2 single crystal used in this study came from a batch where a residual resistance ratio $(\mathcal{R}\equiv\rho(300°\mathrm{K})/\rho(1.1°\mathrm{K})$ of 81 was measured on another crystal used for magnetoresistance measurements.[5] This sample had dimensions of approximately 1 mm on a side and was used as grown.

The de Haas–van Alphen measurements were performed by means of magnetic field modulation.[6] The dc magnetic field was generated by a Varian end-compensated superconducting solenoid and fields to 59 kG were used in the measurement. The ac field was generated by

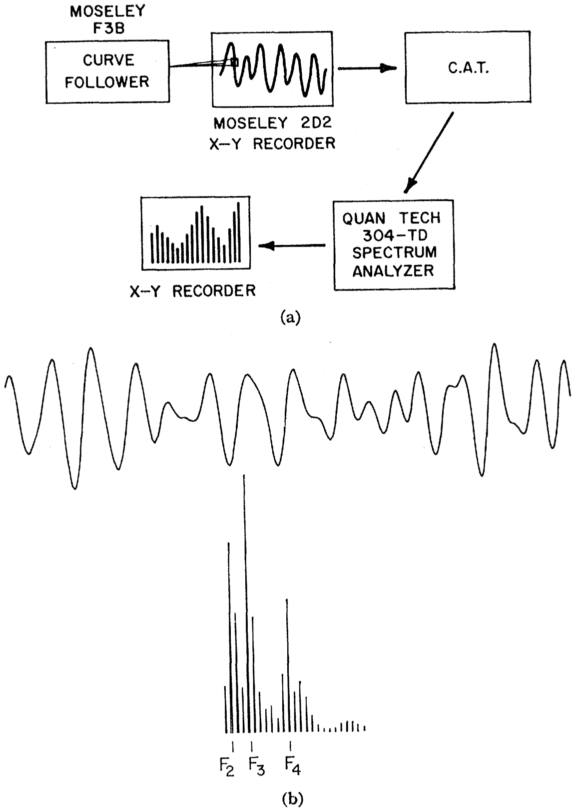

FIG. 1. (a) Block diagram of Fourier-analysis equipment; (b) recorder curve and resulting Fourier analysis.

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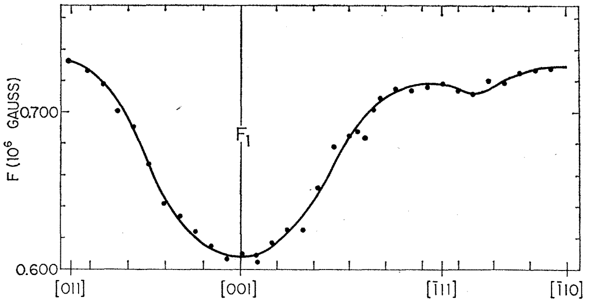

FIG. 2. F_1 as a function of crystal orientation for **H** in the (100) and (110) planes.

means of a copper solenoid coaxial with the superconducting solenoid and mounted on the tail of the Dewar which slipped into the solenoid bore. The ac field had a frequency of 1 kHz and detection was at 2 kHz.

The pickup coil consisted of 2000 turns of Cu wire; 500 turns were used to buck out the induced voltage of the 1-kHz ac magnetic field. This pickup coil was mounted in a Vespel[7] plastic ball. The latter was rotated about a horizontal axis by means of teeth on the perimeter of the ball driven by a spiral gear.[8] The sample was located in the center of the pickup coil.

The output of the pickup coil was fed into a series LC circuit tuned to 2 kHz,[9] and the output voltage across the inductor was fed into a low-noise Techtronix preamplifier model No. 122, the output of which went to an EMI phase-sensitive detector operating in the second-harmonic mode. The output of the EMI drove the Y axis of a Moseley 2D2 X-Y recorder. The X axis was driven linearly in time, as was the current through the superconducting solenoid.

The oscillations thus recorded were Fourier analyzed. These curves were read by means of a Moseley line-follower F3B and the resulting voltage generated by the remote wiper arm of the recorder, which was part of a voltage-divider network was sent into a C.A.T.[10] The purpose of the C.A.T. was to record this curve and in turn, feed it out at a 17-cycle repetition rate into a Quan-Tech Model 304-TD wave analyzer. Approximately 15 cycles of the predominant oscillation of the signal were chosen for the extent of the data. The output of the wave analyzer was recorded on the Y axis of an X-Y recorder. The frequency of the wave analyzer was recorded on the X axis. Figure 1(a), shows the block diagram of this equipment, and Fig. 1(b) shows a typical curve and its Fourier analysis.

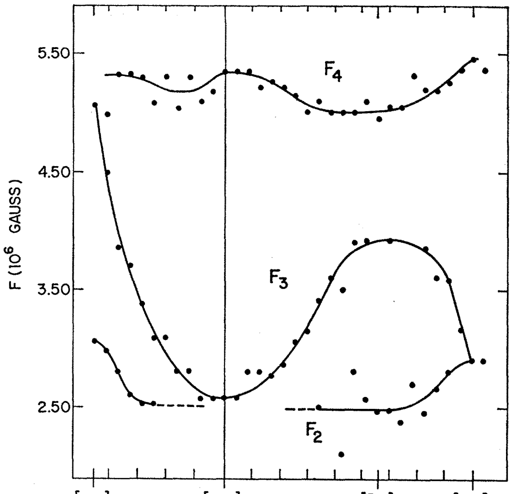

FIG. 3. F_2–F_4 as a function of crystal orientation for **H** in the (100) and (110) planes.

The de Haas–van Alphen measurements were taken with H rotated in two major crystallographic planes of the sample, (100) and (110). The frequencies observed were divided into six groups[11] and are shown in Figs. 2–4 as a function of crystal orientation. In general, the observed de Haas–van Alphen signals were complicated,

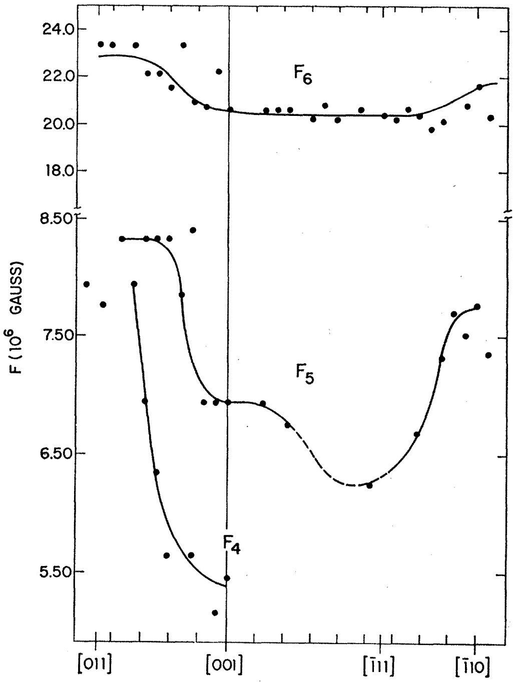

FIG. 4. F_5 and F_6 as a function of crystal orientation for **H** in the (100) and (110) planes. F_4 high-field characteristics as a function of crystal orientation in the (100) plane.

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[7] "Vespel" (SP-2) is a Du Pont registered trademark for polyimide resin containing graphite to reduce friction.

[8] A. C. Thorsen and T. G. Berlincourt, Rev. Sci. Instr. 34, 435 (1963).

[9] When the pickup coil is at the temperature of liquid He, the Q of the circuit is approximately 100.

[10] The C.A.T. is a digital computer manufactured by Technical Measurement Corporation with a 400-channel memory. The computer was used principally as a frequency converter, i.e., our recorder curve was fed into the C.A.T. in a 3-min time interval and fed out at 17 cycles/sec.

[11] These groups do not necessarily designate separate frequency branches but are used as an aid in following the measured frequencies as a function of crystal orientation.

and different groups were emphasized by recording data at different dc magnetic field strengths.

Results

The six de Haas–van Alphen groupings are designated F_1 to F_6.

F_1—The data were taken at a mean magnetic field value of 6 kG; in this field range this oscillation completely dominated the signal and no Fourier analysis was performed. With H in the (100) plane, F_1 has its smallest value of 6.08×10^5 G at [001],[12] peaking at [011] with a value of 7.30×10^5 G. At [011] and in an angular region of approximately 6° on either side of [011], the amplitude of F_1 falls to very small values. At [011], another signal was observed with a frequency of 9.02×10^5 G. With H in the (110) plane F_1 has its smallest value at [001], increasing to a local maximum of 7.18×10^5 G, near [$\bar{1}$11], and has its maximum value at [$\bar{1}$10]. The signal falls to a low amplitude approximately 34° from [001] in the (110) plane.

As the frequency of this group follows the crystal symmetry, F_1 can be associated with a single branch. The mass of the carriers giving rise to this branch is $0.13m_e$ at [001] and $0.16m_e$ at [$\bar{1}$11], m_e being the mass of the free electron.[13]

Figure 2 shows the measured frequencies of this branch as a function of magnetic field orientation for H in the (100) and (110) planes.

F_2, F_3—The frequency difference between these groups is 5% at [001], the difference in frequency increasing away from this orientation. The predominant frequency has the value of 2.57×10^6 G at [001]. Within 30° from [001] the electronic Fourier analysis could not resolve the two groups. In this angular range F_2 and F_3 were resolved by counting the beats in the signal. In the (100) plane F_3 increases monotonically to 5.1×10^6 G at [011], and F_2 increases monotonically to 3.06×10^6 G at [011]. In the (110) plane F_3 increases to a maximum value of 3.9×10^6 G near [$\bar{1}$11], decreasing to 2.9×10^6 G at [$\bar{1}$10]. At [$\bar{1}$10] F_2 and F_3 cannot be resolved. In the (110) plane F_2 increases monotonically from [001] to [$\bar{1}$10].

F_2 can be associated with a single branch as it follows the crystal symmetry. F_3 is composed of more than one branch as [011] and [$\bar{1}$10] are equivalent crystal directions and the frequencies measured for these two orientations are not the same. This is due to the pickup coil orientation relative to H being different along these two directions; consequently, different branches are emphasized.

The mass of the predominant group at [001] is $0.26m_e$.

Figure 3 shows the electronically Fourier-analyzed frequencies of these two groups. Unambiguous frequencies only are shown.[14]

F_4—In the (110) plane F_4 has a minimum value of 5.02×10^6 G near [$\bar{1}$11] increasing to 5.35×10^6 G at [001] and 5.47×10^6 G at [$\bar{1}$10]. In the (100) plane the frequency of F_4 as a function of magnetic field orientation is dependent on the magnetic field strength at which the signal is measured. F_4 has a minimum frequency of 5.2×10^6 G in this plane when H has a value of approximately 13 kG, as is illustrated in Fig. 3. When the measurement was taken at a mean value of H of 44 kG, F_4 at [001] had a value of 5.4×10^6 G increasing to 7.8×10^6 G, approximately 15° away from [011]. F_4 could not be resolved from F_5 within 15° of [011]. Figure 4 shows this high field behavior of F_4.

As the frequency of F_4 (at lower values of H) is consistent with the crystal symmetry it can be associated with a single branch.

The effective mass of the carriers associated with this branch at [$\bar{1}$11] is $0.26m_e$.

F_5—In the (100) plane F_5 has the value 6.9×10^6 G at [001], increasing to 8.2×10^6 G at [011]. In the (110) plane F_5 has a maximum value of 7.7×10^6 G at [$\bar{1}$10] and a minimum value of 6.3×10^6 G near [$\bar{1}$11]. The angular dependence of F_5 is shown in Fig. 4.

As F_5 does not have the same frequency value at [011] and [$\bar{1}$10], more than one branch must be associated with this group.

The effective mass of the carriers associated with F_5 at [$\bar{1}$10] is $0.33m_e$.

F_6—This group was most pronounced at the highest fields of measurement. In the (100) plane F_6 increases monotonically from the value of 20.5×10^6 G at [001] to 23.4×10^6 G at [011]. For H in the (110) plane F_6 is relatively flat and increasing towards [$\bar{1}$10]. No mass measurements were taken on this group (which seems to be associated with a single branch). The angular dependence of F_6 is shown in Fig. 4.

Discussion

The six groups of de Haas–van Alphen frequencies observed indicate that the Fermi surface of SiP_2 consists of several sheets. The change in character of F_4 in the (100) plane when measured at low and high values of H would indicate that magnetic breakdown is occurring at the higher field values. The frequencies measured, 6.08×10^5–23.4×10^6 G, are more characteristic of a metal than a semimetal. In particular, F_6 is associated with a volume in k space containing a total of 6.4×10^{-2} electrons of both spins. The magnetoresistance measurement (Appendix) indicates that SiP_2 is a compensated conductor ($\Delta\rho/\rho_0\propto H^n$, where n lies

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[12] Indicated crystal orientations are for the experimental condition that H is parallel to this orientation.

[13] Masses were measured for those orientations where one branch greatly predominated the signal. The mass was determined by the amplitude variation of the signal with temperature, at a given value of magnetic field.

[14] In the Fourier-analysis sum, difference and harmonic frequencies are present. Only those frequencies are considered physically real which can be continuously followed as a function of orientation and which are not sum, difference, or harmonics of other branches.

between 1.4 and 1.6). The compensated characteristic would be expected, as there are four molecules of SiP_2 per unit cell.

The sixfold coordination of Si (as described in the introduction) is unusual. Such coordination for post-transition metals is conventionally interpreted by assuming sp^3d^2 hybridization in which the d orbitals, usually too high in energy for bonding, mix with the s and p orbitals. In contrast, for transition metals, the d orbitals lie lower in energy than the s and p, and octahedral hybridization is designated as d^2sp^3. The fourfold, tetrahedral coordination of the P atoms involve the common sp^3 hybridization.

If such a scheme is assumed, a one-electron, one-molecule, molecular orbital diagram may be constructed (Fig. 5) in a manner like that described for the transition-metal pyrite compounds.[15] Such models, while only qualitative, have been of use in other systems[16] for explaining electrical properties.

The d orbitals having octahedral symmetry (e_g) are used in the hybridization. Since σ bonding should be stronger than π bonding because of greater degree of overlap, the t_{2g} orbitals which might take part in π bonding are considered nonbonding. The six states of the Si are combined with six from the P atoms forming the valence band, which contains 12 electrons. The remaining two electrons fill the single state of the P-P pair. An electron pair or σ bond, thus, exists along the direction of every bond and the valence band is completely filled. The material would be expected to be a semiconductor. Since it shows metallic conduction, it is assumed that the energy separation ΔE is zero and electrons from the bonding band may transfer to the antibonding band without an energy barrier. This overlap is consistent with the compensated magnetoresistance behavior of SiP_2. Optical data would be a useful independent test of the validity of the above model and a more extensive measurement than previously reported[1] is now being performed.[17]

If the sp^3d^2 hybridization is the wave character of the carriers, the measured effective masses of the carriers associated with the observed de Haas-van Alphen frequencies ($0.13m_e$ to $0.33m_e$) would indicate relatively small d character in these wave functions, as d-band carriers generally have masses near or larger than the mass of the free electron. This also indicates that there is essentially no contribution of the t_{2g} orbitals to the conduction bands.

In summary, we can say that SiP_2 is a compensated metallic conductor with little d-band characteristic associated with the carriers involved in the conduction process.

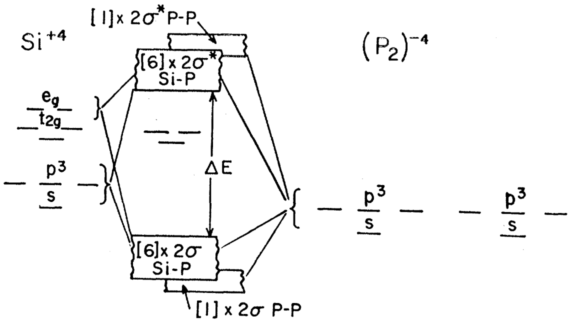

FIG. 5. Schematic one-electron one-molecule energy-level diagram for SiP_2. The notation $[6]\times 2\sigma$ Si-P represents six σ bonds between Si and P, each occupied by 2 electrons. The notation $[1]\times 2\sigma$ P-P represents one σ bond between two P atoms occupied by 2 electrons. The notation * represents antibonding orbitals.

ACKNOWLEDGMENTS

We wish to thank J. Moore for help in taking the data and F. Fountain for use of his equipment in Fourier analyzing our data.

APPENDIX: TRANSVERSE MAGNETORESISTANCE

The magnetoresistance of a randomly oriented crystal was measured. This crystal was from the same batch as the crystal used in the de Haas-van Alphen measurement, with $\mathcal{R}$ of 81. The maximum $\Delta\rho/\rho_0$ at 46 kG was 8.4. $\Delta\rho/\rho_0$ is proportional to H^n at the highest fields with $1.4 \leqq n \leqq 1.6$ for different crystal orientations. Figure 6 shows the transverse magnetoresistance as a function of orientation.

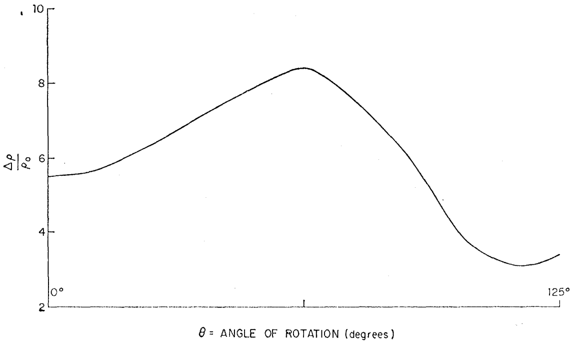

FIG. 6. Transverse magnetoresistance of SiP_2 as **H** is rotated in an arbitrary plane perpendicular to I, with $H=46$ kG, $T=1.4$°K.

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