de Haas–van Alphen Effect in Superconducting V_3Si

F. M. Mueller
Center for Materials Science, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

D. H. Lowndes and Y. K. Chang
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

A. J. Arko and R. S. List [(a)]
Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 17 September 1991)

Quantum oscillations in the magnetization, periodic in inverse field (de Haas–van Alphen effect), have been observed in V_3Si both above as well as *below* the superconducting critical field B_{c2} of 17.95 T for fields along the [100] direction and at 1.5 K. The oscillations have the same frequency ($\pm 0.3\%$) in the two field regimes. It is shown by intercomparing the amplitudes that quantum oscillation measurements can be used to determine the field density distribution in the superconducting phase.

PACS numbers: 71.25.Hc, 74.70.Cf

The de Haas–van Alphen (dHvA) effect [1] is the oscillatory component of the diamagnetic susceptibility of a metal. It is a result of two basic quantal properties of electrons, namely, the quantization of their orbital motion in an applied magnetic field [2–4] and the existence of a Fermi surface (a consequence of their spin-$\frac{1}{2}$ statistics, i.e., of the Pauli principle). Historically, the dHvA effect has been extremely important in providing the most detailed, comprehensive information about the size and shape of the Fermi surfaces of metals and many intermetallic compounds [5], and a direct measure of the orbitally averaged electronic scattering rate [6].

The conventional Lifshitz-Kosevitch derivation [1,7] of the dHvA effect has implicitly assumed that one is dealing with a metal in the normal (nonsuperconducting) state. However, the quantization condition appears to be so general as to apply also to a type-II superconductor in the mixed or vortex state. As in the Aharonov-Bohm (AB) effect [8], the magnetic flux is quantized via a line integral

$$(2e/\hbar)\int \mathbf{A}\cdot ds = 2\pi n\,, \tag{1}$$

where n is the quantum number and the quantum of flux is $h/e = 4.135704\times 10^{-15}$ Wb [9]. The flux quantization condition (1) is independent of the distribution of flux in the interior of the path integral. The eigenenergies are given by $E_n = (n+\frac{1}{2})\hbar\omega_c$, where the cyclotron frequency $\omega_c = eB/m$.

The implication of this reasoning is that type-II superconductors in the mixed or vortex phase should exhibit a dHvA effect below B_{c2} as well as above. But what is the relationship of the quantum oscillations in the two regimes? In this Letter we examine this question in the case of a standard and well studied type-II *A*15 material, V_3Si, with the magnetic field oriented close to the high symmetry (100) axis. To our knowledge, the results reported here are the first observation of dHvA oscillations *in the vortex state* of an *isotropic, fully three-dimensional material.* The only previous reports of a dHvA effect below B_{c2} were those of Graebner and Robbins (GR) for the hexagonal layered (quasi-2D) chalcogenide 2H-$NbSe_2$ [10], and the recent observations of a dHvA effect in $YBa_2Cu_3O_{7-\delta}$, using oriented powders, by Mueller *et al.*, Smith *et al.*, Fowler *et al.* [11], and by Kido *et al.* [12]. However, the very high B_{c2} value has so far precluded any comparison of dHvA oscillations in the two regimes for high-temperature superconductors.

Our dHvA amplitude data for V_3Si have been analyzed into two distinct fundamental frequencies, which are the same to within $\pm 0.3\%$ in both the normal ($B > B_{c2}$) and superconducting regimes. In contrast, Graebner and Robbins reported a 3% increase in frequency from above to below B_{c2}, for a particular field orientation. However, this frequency shift may have been due to the angle of their magnetic field relative to the crystallographic axis and to the way flux lines penetrate and move in an anisotropic superconductor [13]. Also, 2H-$NbSe_2$ is known to contain a strong charge-density wave, which in other materials has been shown to modify the dHvA frequency and harmonic content [13].

The dynamics of vortex motion has been well characterized in V_3Si through neutron flux lattice measurements [14]. In fact, the single crystal used in the dHvA experiments (discussed below) was cut from the ends of that used in the flux flow experiments. The residual resistivity ratio of the samples was about 30. The V_3Si crystal ingot from which samples were cut was prepared by the rf induction-heated float-zone method at Oak Ridge National Laboratory. Neighboring samples from this same ingot are known from TEM measurements to be free of second-phase inclusions, and previously were characterized extensively via measurements of normal and superconducting phase properties, by observations of the martensitic structural transformation near 21 K, and by observations of neutron diffraction by the flux line lattice in the mixed state [14].

Experiments were carried out at 1.5 K using a field modulation dHvA spectrometer and a 19 T (maximum B induction field) Bittermagnet at the Francis Bitter National Magnet Laboratory. The samples were mounted in a single-plane spiral gear-driven sample rotator, with which samples could be rotated in any crystallographic plane, which could be preselected with a precision of about 1°. An astatically wound pickup coil rotated with the sample; a second, fixed pickup coil contained a gold reference specimen, whose high-frequency "belly" dHvA oscillations were used to locate the most homogeneous field region, as the entire sample holder was translated in a steady B field.

The solid lines in Fig. 1 illustrate dHvA oscillations present both above and below B_{c2} for a V_3Si specimen with H parallel to [100]. The transition to the normal phase begins at about 17.2 T (0.0583 T^{-1}) in the large modulation field used in these experiments. Separate low-modulation measurements showed that the transition to the normal phase was complete at $B_{c2}=17.97$ T in our sample. The noise content of the two portions of Fig. 1 ($H<17$ T and $H>18.2$ T) is the same, but the higher field data have an amplitude about 4 times as large. Above B_{c2}, the oscillations in the normal phase appear to have the same frequency as those observed below B_{c2}, though a precise determination of their frequency is complicated by the occurrence of a beat minimum and by the fact that only about five complete oscillations could be observed between B_{c2} and the maximum H field available. The frequency of the oscillations at [100] is 1.98 (± 0.08) kT, as determined from a plot of oscillation number versus $1/B$. This corresponds to a cross section that is approximately 10% of the Brillouin zone cross-sectional area of 18.55 kT.

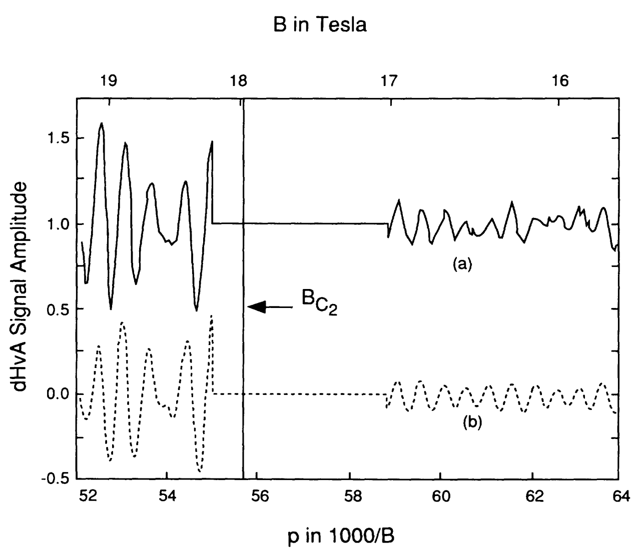

FIG. 1. de Haas-van Alphen amplitude for V_3Si as a function of $1/B$. The solid line is the oscillatory part of the experimental data and the dashed curve is a two-extremal-orbit fit, including all harmonics. As is discussed in the text, the dHvA frequencies are the same in the normal and superconducting phases of V_3Si, within experimental error ($\pm 0.3\%$). The development of the superconducting gap, 2Δ, does not alter the cyclotron frequencies; what is affected are the dHvA amplitudes. Data between 17 and 18 T, reflecting irregular flux motion in V_3Si, are not presented.

Because of the few oscillations observed, we analyzed the amplitude data in the two regimes of Fig. 1 by means of two "slow" Fourier transforms in $1/B$, from which the power spectral densities were calculated. Each transform exhibited two separate peaks. For both regimes, one peak was at about 1.98 kT, consistent with the "number plot" discussed above. Each transform also exhibited a weaker second frequency at about 1.49 kT. To better define the second frequency, and because we wanted an intercomparison of results in the two regimes, we also have made an amplitude analysis using Lifshitz-Kosevitch (LK) theory [7,15].

In these experiments, the slowly varying H field was modulated by ~ 0.1 T (at $H\sim 19$ T) at 50 Hz. Detection was carried out using a phase-sensitive system, tuned to the third harmonic. The dHvA fundamental amplitude was minimized by adjusting the modulation amplitude. This adjustment slightly complicates the amplitude analysis, since we need to calculate the third derivative with respect to B of the LK magnetization for comparisons with the data. For a given set of fitting parameters, we have done this numerically with sufficient precision that the third derivative of the magnetization was accurate to better than 1 part in 10^4. Another experimental concern for the amplitude analysis is that the large modulation amplitude will induce flux flow and screening currents that may reduce the dHvA amplitude. However, flux pinning has been studied in V_3Si in the high-T, low-H and the low-T, moderate-H limits [14], and these measurements can be used to estimate the possible influence of flux flow on the dHvA signal under our experimental conditions. Using a critical state model, the *maximum* value of $\Delta H/\Delta r$ in a 1-mm-diam cylindrical dHvA sample can be estimated from $\Delta H(\mathrm{G})/\Delta r(\mathrm{cm}) \sim (4\pi/10)J_c(\mathrm{A/cm^2})$, using $J_c[H=1\ \mathrm{T},\ T=4.2\ \mathrm{K}]=10^4\ \mathrm{A/cm^2}$, and $J_c \sim B^{-1/2}(1-B/B_{c2})^2$ to scale the calculation to $H=15$ T, near the low end of the range in which we observe dHvA oscillations in the mixed state. This results in $J_c(15\ \mathrm{T})/J_c(1\ \mathrm{T})=0.008$, and a radial variation $\Delta H\sim 4$ G between the outer surface and the center of the V_3Si sample. This variation is negligible relative to the period, $P=H^2/F$, of the dHvA oscillations ($P\sim 1100$ or 1500 G at 15 T), and becomes still smaller with increasing H. This calculation also indicates that diamagnetic hysteresis is small relative to the dHvA period.

Initially each data regime was fitted separately and parameters for the dHvA amplitude, frequency, phase, orbital mass m^*, and Dingle temperature T_D were varied. Different minimalization runs had different numbers of

TABLE I. dHvA frequencies (in kT) for V_3Si above and below B_{c2}.

	Above B_{c2}	Below B_{c2}
1	1.494 ± 0.003	1.498 ± 0.003
2	1.986 ± 0.003	1.987 ± 0.003

base frequencies (along with all of their LK harmonics). We conclude that two independent frequencies (with their harmonics) are well supported by these data. In Table I we show results for the two frequencies, fitted separately above and below B_{c2}. Although there is a slight shift upward in frequency in these data, similar to that seen in GR, we think it is barely statistically significant. The increase seen here is less than 0.3% (and for only one orbit), whereas that in GR was 3.0%. This point is significant for theoretical interpretations of the origin of the dHvA effect below B_{c2}, since most theories [16–19] find that the orbital Landau level spacing is modified to become $(E_n^2+\Delta^2)^{1/2}$. Assuming a mass m^* of 2.1 free electron masses and a field of 18 T, $\hbar\omega_c$ is 1.59×10^{-22} J. From the observed dHvA frequency we see using the semiclassical approximation that near 18 T the fourteenth Landau level is the one contributing to the dHvA effect in V_3Si. Assuming that $2\Delta/kT_c$ is about 4.2, then Δ is 1.19×10^{-22} J. At the lowest field shown in Fig. 1, Δ is about 56% of its zero field value. Using the $(E_n^2+\Delta^2)^{1/2}$ formula for the energy scale implies a frequency shift there of about 3.5% between normal and superconducting phases, reducing for higher fields to zero shift at B_{c2}. Since the two observed frequencies are invariant on a scale of 0.3%, we conclude that a theory is needed that includes effects both beyond the semiclassical approximation and taking into account vortex-order parameter nonlinearities. Such theories are being actively pursued by a number of groups.

The data of Fig. 1 and the analysis of Table I suggest that the frequencies in the two regimes are almost invariant. However, there *is* a significant change in the dHvA oscillation amplitude. Close examination of Fig. 1 suggests that the oscillation amplitude below B_{c2} is about one-fourth of that above, and that this one-fourth factor is itself ***nearly invariant*** with field over the observed regime below B_{c2}. Initially, these facts were quite puzzling to us, since the superconducting order parameter must be rapidly varying close to B_{c2}.

To understand these data we have applied the theory of the mixed phase as developed originally by Abrikosov [20] and most recently in several papers of Brandt and co-workers [21]. Mostly this latter work focused on determining the effective distribution of fields in the mixed state, so as to make comparisons with NMR and muon-spin-resonance experiments. In the case of V_3Si at low temperature and for a field close to B_{c2} applied along a high symmetry axis, the field distribution can be obtained fairly simply. We express the field as $p=100/B$ rather than using B itself. [21]. For fluxoids in a perfect V_3Si crystal, the field distribution function $N(p)$ exhibits both the jump singularities and logarithmic divergences of different two-dimensional van Hove singularities [21]. These distributions are not only integrable, but they have convergent Fourier developments as

$$N(p)=\int A(\tau)\cos(\tau p)d\tau\ , \tag{2}$$

where τ is the Fourier development of p. Such expansions are familiar from the moment-singularity method for electronic density of states developed by Lax and others in the mid-1950s [22]. The upshot of that work was that any density of states can be characterized by its critical structure or by its moment expansions.

For simplicity we will make here a reasonableness argument; however, all of the numerical results discussed below actually used full expressions, numerical third derivatives, etc. Instead, let us expand the sinh function of the LK amplitude as an exponential, ignore all field dependence of the dHvA amplitude except for the sinusoidal variation, ignore both the Onsager phase and the min/max LK phase parameter, and not take the third derivative of the magnetization with respect to field [15]. The rth dHvA harmonic oscillatory magnetization in the normal phase above B_{c2} is then given by

$$\tilde{M}_r=CT\sin[2\pi r(Fp)]\exp[-arm^*(T+T_D)p]\ , \tag{3}$$

where we have used $p=100/B$. (Note that in all we use only the positive half of the p space.) By averaging $\tilde{M}_r$ over the distribution function of Eq. (2), we obtain the amplitude in the superconducting phase:

$$\langle\tilde{M}_r\rangle=\int dp\,\tilde{M}_r\int A(\tau)\cos(p\tau)d\tau\ . \tag{4}$$

The p integral in Eq. (4) has a closed form. What we see then is that the measured amplitude [the left-hand side of Eq. (4)] is given as a convolution of the density distribution function $A(\tau)$ and a function with simple poles in the complex plane. Hence, it is possible to invert Eq. (4) [23].

This means that, within LK theory, the measurement of dHvA amplitudes above and below B_{c2} can be used to determine the form of the field distribution density. That is, the phase smearing of dHvA amplitudes by the inhomogeneous field in the mixed phase of type-II superconductors can be used to determine the field inhomogeneity. Since this inversion procedure devolves into taking a numerical inverse Laplace transform of data in the general case, and this can be ill conditioned, we have made only a modest development of $N(p)$ here. In particular, we have assumed a shape for $N(p)$ similar to that given by Brandt's numerical solution of the GL equations [21], using measured values of the coherence length and GL parameter $\mathcal{K}$, but we have added parameters for the maximum and minimum fields. These were then used to calculate a LK $\tilde{M}$, the third numerical derivative was taken,

TABLE II. Parameters for the field distribution density in V_3Si at $H=17.5$ T ($\mathcal{K}=20$, $\lambda=190$ nm).

	Lowest field (T)	Highest field (T)
Brandt (Ref. [21])	17.23	17.61
This work	17.25 ± 0.01	17.59 ± 0.01

and this result was compared in a least-squares sense with the measured dHvA signal. The resulting fields were nearly identical with those predicted by the GL equations. These results are summarized in Table II.

Using these results, we obtain an answer to the amplitude question raised earlier. Below B_{c2} the form of the distribution function we have used is nearly invariant over the field range used in these experiments. Hence, we see that this distribution function moves with the average field, but that its width over the same region is roughly fixed. Using the idea of phase smearing, this implies that the dHvA amplitudes are diminished by a constant Dingle temperature [15,16]. Hence, the observed dHvA amplitude is diminished *by a roughly constant factor, as observed here for* V_3Si, *and as was observed also in the* 2*H*-$NbSe_2$ *experiments of GR* [10].

In summary, we have observed dHvA oscillations above and below B_{c2} in the isotropic, fully three-dimensional *A*15 material V_3Si. We find no statistically significant change in dHvA frequency in the normal and mixed superconducting states, in contrast to the only other such measurement [10]. Finally, our analysis explains the approximately constant amplitude-reduction factor that is observed when going from above to below B_{c2}, and our experiments demonstrate that it is possible to use quantum oscillation measurements for direct determinations of the field probability density of superconductors in external fields $B < B_{c2}$.

We would like to thank B. Brandt and L. G. Rubin for support in the development of experimental facilities at the Francis Bitter National Magnet Laboratory. We thank B. Klein for providing unpublished results of calculations of Fermi surface structures for V_3Si. We thank L. J. Campbell, L. Daemen, P. Kumar, and V. Kogan for discussions on flux lattices. We are especially grateful to L. Daemen for providing us with the probability density program that was used to calculate the distribution used in Eq. (2). One of us (F.M.M.) would like to acknowledge J. B. Ketterson for some lengthy helpful discussions on the technique of vector field modulation. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., at Oak Ridge National Laboratory, and under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, at Los Alamos National Laboratory.

Note added.—Y. Onuki *et al.* [J. Phys. Soc. Jpn. **61**, 692 (1992)] recently confirmed GR's observation of dHvA oscillations in the mixed state of 2H-$NbSe_2$.

[a]Current address: Central Research Laboratories, Texas Instruments Inc., Dallas, TX 75265.

[1] A. V. Gold, in *Solid State Physics*, edited by J. F. Cochran and R. R. Haering (Gordon and Breach, New York, 1968), p. 39.

[2] L. Landau, Z. Phys. **64**, 629 (1930).

[3] E. Teller, Z. Phys. **67**, 311 (1931).

[4] A. B. Pippard, in *Solid State Physics* (Ref. [1]), p. 6.

[5] See, for example, *Electrons at the Fermi Surface*, edited by M. Springford (Cambridge Univ. Press, Cambridge, 1980), Chaps. 5–8, 11.

[6] R. B. Dingle, Proc. R. Soc. London A **211**, 517 (1952); D. H. Lowndes, K. Miller, and M. Springford, Phys. Rev. Lett. **25**, 1111 (1970); see also *Electrons at the Fermi Sea* (Ref. [5]), Chaps. 9 and 10.

[7] I. M. Lifshitz and A. M. Kosevich, Zh. Eksp. Teor. Fiz. **29**, 730 (1955) [Sov. Phys. JETP **2**, 636 (1955)].

[8] Y. Aharonov and D. Bohm, Phys. Rev. **115**, 485 (1959).

[9] Note that this is twice the perhaps more familiar superconducting flux quantum.

[10] J. E. Graebner and M. Robbins, Phys. Rev. Lett. **36**, 422 (1976).

[11] F. M. Mueller, C. M. Fowler, B. L. Freeman, W. L. Hults, J. C. King, and J. L. Smith, in Proceedings of the Conference on Electronic Structure in the 1990's, Bad Honnef, Germany, 22–26 July 1990 (to be published); J. L. Smith, C. M. Fowler, B. L. Freeman, W. L. Hults, J. C. King, and F. M. Mueller, in the Third International Symposium on Superconductivity, Sendai, Japan, 6–9 November 1990 (to be published); C. M. Fowler *et al.*, Phys. Rev. Lett. **68**, 534 (1992).

[12] G. Kido, K. Komorita, H. Katayama-Yoshida, T. Takahashi, Y. Kitaoka, K. Ishida, and T. Yoshitomi, in the Third International Symposium on Superconductivity (Ref. [11]).

[13] See, for example, S. Doniach, in *High Temperature Superconductivity*, edited by K. S. Bedell *et al.* (Addison-Wesley, New York, 1990).

[14] D. K. Christen *et al.*, Physica (Amsterdam) **107B&C**, 301 (1981); D. K. Christen *et al.*, IEEE Trans. Magn. **19**, 884 (1983).

[15] See also D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge Univ. Press, New York, 1984).

[16] K. Maki, Phys. Rev. B **44**, 2861 (1991).

[17] M. J. Stephen, Phys. Rev. B **43**, 1212 (1991).

[18] R. S. Markiewicz, I. D. Vagner, P. Wyder, and T. Maniv, Solid State Commun. **67**, 43 (1988).

[19] H. Akera, A. H. McDonald, S. M. Girvin, and M. R. Norman, Phys. Rev. Lett. **67**, 2375 (1991).

[20] A. A. Abrikosov, Zh. Eksp. Teor. Fiz. **32**, 1442 (1957) [Sov. Phys. JETP **5**, 1174 (1957)].

[21] See, for example, E. H. Brandt, J. Low Temp. Phys. **73**, 355 (1988), and references therein.

[22] M. Lax and J. Lebowtiz, Phys. Rev. **96**, 594 (1954); H. B. Rosenstock, Phys. Rev. **97**, 290 (1955).

[23] A. Mushkulavilli, *Singular Integral Equations*, translated by G. M. Volkoff (Interscience Publishers, New York, 1962), 2nd revised translation.