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de Haas–van Alphen Effect in the High-T_c $A15$ Superconductors Nb_3Sn and V_3Si

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de Haas–van Alphen (dHvA) oscillations have been observed in Nb_3Sn in the (110) plane and in V_3Si at two orientations using single crystals of high resistance ratio and magnetic fields in excess of H_{c2}. The dHvA frequency data for Nb_3Sn can be interpreted as a series of nested ellipsoids centered at M, as suggested by a recent high-precision calculation of the Nb_3Sn Fermi surface.

We present the first de Haas–van Alphen (dHvA) measurements of the Fermi surfaces of high-T_c $A15$ structure superconductors, with measurements for both Nb_3Sn and V_3Si. We compare the Nb_3Sn results to a recent band-structure calculation[1] and find good agreement. The upper critical fields, H_{c2}, are ~20 kOe lower than earlier measurements,[2] apparently due to the high-purity single crystals of Nb_3Sn and V_3Si used.

The current high level of interest in $A15$ materials is due to the recent and continuing discoveries of the coexistence of a variety of anomalous normal-state properties[3] at both high and low temperatures, with the highest-T_c materials showing the most puzzling behavior. It is widely felt that the underlying physical features leading to these unusual normal-state properties are also the cause of the high transition temperatures observed in many $A15$-structure materials. A variety of physical models ascribing special features to either the phonon or electron distributions have been invoked to explain the normal-state properties. Our results are a first step in providing a microscopic test of the various electronic models.

Unfortunately, the very properties which make the high-T_c $A15$'s such interesting materials had until now, combined to prevent dHvA measurements of the Fermi surface; the only prior dHvA measurements being the very recent results of Arko, Fisk, and Mueller[4] for Nb_3Sb (T_c ~0.2 K). Magnetothermal oscillations were previously observed in V_3Ge.[5] The main limiting experimental factors are the following: (1) Effective masses are expected to be high because of the intrinsically flat electronic band structure and because of the strong electron-phonon coupling ($\lambda \sim 1.4$ for Nb_3Sn). (2) H_{c2} is large, so that exceptionally high magnetic fields are needed simply to reach the normal state. (3) The materials tend to have high residual (and intrinsic) resistivities[6] so that T_D, the Dingle temperature, would be expected to be large. (4) Some of the most interesting materials undergo a martensitic transformation so that the dHvA signal is suppressed due to interference of oscillations and to phase smearing between tetragonally distorted subdomains.

The Nb_3Sn crystals were grown over a period of four months by closed-tube vapor transport with iodine as the transporting agent. X-ray dif-

fraction on part of the deposit showed only sharp lines of the $A15$ structure with a room-temperature lattice parameter of 5.290 Å. An inductive measurement of the actual dHvA crystal showed a T_c (midpoint) of 17.8 K and a width (10%–90%) of 0.07 K. Resistivity measurements confirm that the samples undergo a martensitic transformation at 51 K. We estimate that $R(300\ \mathrm{K})/R(0\ \mathrm{K}) = 50$ assuming that T^2 is a satisfactory extrapolation function.[6,7] The V_3Si specimen was grown using a floating-molten-zone technique with induction heating in a pure-argon atmosphere. No resistance ratio or T_c measurements were made. However, from the amplitude of the dHvA signals we estimate the purity to be at least comparable to that of Nb_3Sn.

Oriented single-crystal samples were mounted in a spiral-gear-driven rotator. The accuracy with which orientations are known in the (110) plane is estimated to be about 1°.

The experiments were conducted in the 400-kOe "slow-pulsed-field" facility at the University of Amsterdam.[8] The principal advantage of a slow magnetic field pulse is that self-heating and signal-detection problems associated with eddy currents in metallic samples are avoided and mechanical vibrational noise is minimized. All dHvA data were taken in the free-inductive-decay mode from 400 kOe in order to eliminate electrical noise introduced through the current-regulating circuits. The entire system was checked by observing dHvA oscillations in a single crystal of Mg; the results agreed with published values of Mg dHvA frequencies to within 1–3%.

The output of a compensated dHvA pickup coil was differentiated twice, filtered to take out some of the slowly varying voltage resulting from incomplete coil compensation, amplified, and displayed directly on the recorder. A typical recorder tracing is shown in Fig. 1. Since the induced voltage in the dHvA pickup coil is directly proportional to the time frequency of the dHvA oscillations, the usual exponential amplitude increase as H increases will not be observed due to the $1/H$ periodicity of the dHvA oscillations. For low-mass, low-frequency oscillations one may even see an amplitude decrease, which is further accentuated by the dc filter. This decrease in amplitude is clearly evident in Fig. 1.

The dHvA oscillations were analyzed by marking the positions of successive oscillation peaks and making a plot of oscillation number versus $1/H$; the slope of this "number plot" gives the dHvA frequency directly and was generally found to be a good straight line, giving us confidence in our field calibration. Beat structure, while obviously present at some orientations, was difficult to resolve because of the few oscillations

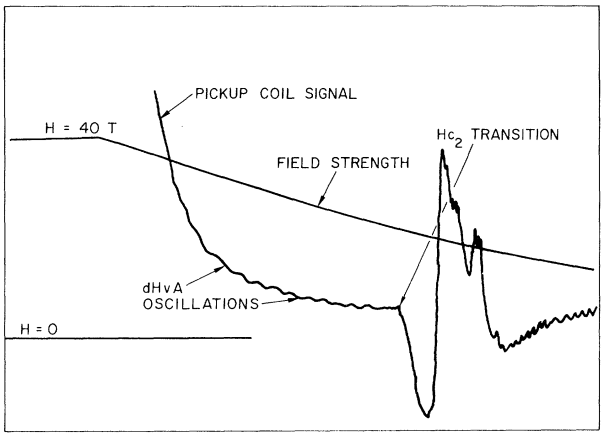

FIG. 1. Dual traces of a typical high-speed chart recording for Nb_3Sn at 75° from [100] showing the decay of a 40-T magnetic field pulse and the simultaneous recording of dHvA oscillations followed by the superconducting transition at H_{c2} vs time (the field decays from 40 T to H_{c2} in about 0.15 sec). The apparent oscillations below H_{c2} are noise generated in the pickup coil in the superconducting state due to eddy currents, flux jumps, etc., and are *not* periodic in $1/H$.

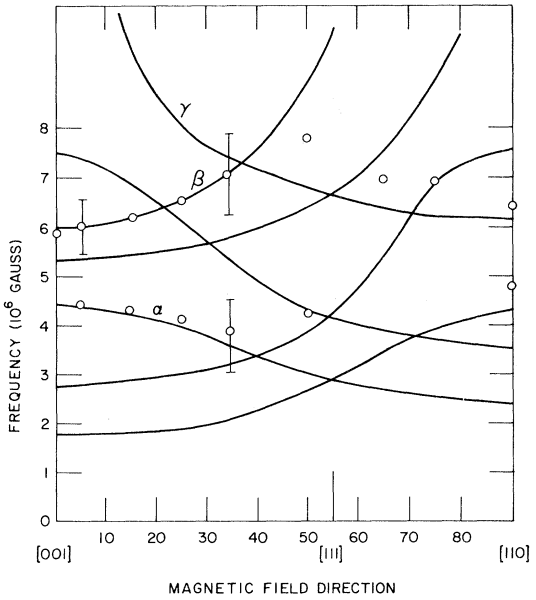

FIG. 2. dHvA frequencies for Nb_3Sn in the (110) plane. The solid circles (with typical error bars) are the experimental results. The solid lines are generated from the Fermi-surface model and band-structure calculation of Ref. 1.

plus the above-mentioned problems with the amplitude dependence. Nevertheless, it is possible to resolve several separate branches in the Nb_3Sn data. Figure 2 displays the dHvA frequencies (open circles) found for Nb_3Sn in the (110) plane, while the limited data for V_3Si are given in Table I. The long cooling time of the magnet (~4 h after each pulse) made it necessary to space data at only 10° intervals. The typical error estimates indicated in Fig. 2 are conservative, based on a maximum possible counting error of one-half oscillation. The reproducibility of the dHvA frequency measurements at a given orientation was a few percent. There was evidence in the raw data for additional dHvA frequencies, both larger and smaller than those presented in Fig. 2. However, the signal-to-noise ratio for these oscillations is barely greater than 1; so they are not included here.

To interpret our results we have used the band calculation of Ref. 1. The calculation is similar to that of Mattheiss[9] (i.e., augmented-plane-wave method used with a *non*-self-consistent overlapping charge-density model, and Slater $\alpha = 1$ exchange) except that non–muffin-tin terms were included, and much greater precision was maintained throughout (i.e., 56 points in $\frac{1}{48}$th of the zone versus Mattheiss's 4, 3-mRy convergence versus 30 mRy, etc.). The solid lines in Fig. 2 are the predicted theoretical frequencies from Ref. 1. The correspondence between the observed frequencies and those labeled α, β, and γ is good. Based on this we conclude that the observed frequencies are consistent with a set of nested ellipsoids at M, similar to the observations in Nb_3Sb[5] and V_3Ge.[6,9] (This conclusion is not reached from the data alone.) Since very low dHvA frequencies are discriminated against in pulsed-field experiments as discussed above, it is reasonable that we do not observe the (low-mass) lowest predicted branches in Fig. 2. Other larger "missing" orbits have too high a mass ($m_{\mathrm{exp}}{}^* \sim 2.4 m_{\mathrm{band}}$) to be observed with this relatively insensitive technique. Further, the frequencies bunched near 5×10^6 G are too closely spaced to allow a clear resolution of beats. Within these limitations there is excellent agreement between our data and the predictions of the theory of Ref. 1. While the symmetry of the experimental frequencies is ambiguous, the magnitude is not. Several other band calculations[3,9,10] predict surfaces too large to fit our data, although it was pointed out that the size of small pieces is quite sensitive to the exchange approximation.[10]

TABLE I. dHvA frequencies for V_3Si.

Orientation	Frequency (10^6 G)
[100]	6.24
	4.60
[110]	7.78

We have indirectly and simultaneously measured the anisotropy of the upper critical field H_{c2} for Nb_3Sn at the same 10° intervals. Taking the highest-field point of the normal-to-superconducting transition (H decreasing) as defining H_{c2}, we find that $H_{c2} = 214$ kOe (at $T = 1.5$ K) and is isotropic within the 1% precision of our measurements. (For V_3Si we find $H_{c2} = 216$ kOe at $T = 1.5$ K.) This result is significantly smaller than the earlier (extrapolated) value of 240 kOe at $T = 0$ or $H_{c2} = 235$ kOe at $T = 1.5$ K. We have ruled out that this difference is due to extrinsic effects. Instead, we believe that the lower H_{c2} is intrinsic to the highly perfect (and well annealed) single crystals used. Evidence to support this comes from the fact that a poorer Nb_3Sn specimen, which gave only weak lower-frequency dHvA oscillations, had a higher critical field ($H_{c2} \sim 230$ kOe along [100]) and also displayed some slight anisotropy of H_{c2} (slightly lower values elsewhere), consistent with literature values.[2]

A significant concern for future dHvA experiments on Nb_3Sn may turn out to be the effect of thermally cycling a single crystal through the structural transformation. Repeated thermal cycling decreased the dHvA amplitudes by at least a factor of 2. These were restored by annealing at 700°C for five days. Our data do not yet allow us to determine which factor (high T_D, phase smearing, changes in electronic structure) is primarily responsible for the signal degradation. The change in the lattice parameter accompanying the transformation is only of order 1% so that a major change in the band structure is not expected. It does seem, however, that it may be possible to use the dHvA effect as a detailed probe of the electronic consequences of the $A15$ structural transformation and defect formation.

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Mo(001) Surface: A Self-Consistent Calculation of the Electronic Structure

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A self-consistent pseudopotential calculation for an unrelaxed Mo(001) surface reveals strong surface states and resonances. The results are used to interpret the sharp peak structure near the Fermi level and other structures measured by recent angle-resolved photoemission experiments. The structure is attributed uniquely to surface states and resonances. Contrary to other proposals, relativistic, many-body, and surface-contraction effects are not necessary to explain the observed spectra.

Recent photoemission experiments applied to the (001) face of molybdenum[1-4] reveal two sharp peaks which are located around 0.3 and 3 eV below the Fermi level. Their large sensitivity to surface contamination[1-3] suggests that their origin is due to surface resonances or surface states. Moreover, angle-resolved photoemission experiments reveal that the peak near the Fermi level has its maximum for normal emission, but does not disappear when the emission angle is increased. In addition a second peak appears slightly below the high-lying resonance for larger emission angles.[4]

Theoretically, there has been some controversy about the origin and interpretation of the sharp structures as surface states or resonances. Noguera *et al.*[3] identified the upper peak due to normal emission as a combination of a surface resonance and a *d*-band edge around the Γ point of the two-dimensional Brillouin zone. In order to place the energy of this resonance at the energy of the experimental peak they had to include a 10% to 13% inward relaxation of the surface layer.

Using a nonrelativistic tight-binding Green's-function method Weng and co-workers.[2,4] predicted the occurrence and the dispersion of three occupied surface resonances away from normal emission in satisfactory agreement with the experimental results; however, they were not able to explain the existence of a strong resonance at normal emission.[5] They argued that it might be due to relativistic effects. It should be stressed that none of the above theoretical calculations treated the redistribution of the electrons at the surface self-consistently. Noguera, Spanjaard, and Jepsen[6] argued from the similarity of the total charge density at the surface as compared to the bulk charge density that self-consistency plays a minor role at transition-metal surfaces. They therefore used screened muffin-tin potentials obtained from a self-consistent bulk calculation also for the surface atoms. We have found that for self-consistency the screened potential around a surface atom must differ considerably from the corresponding potential around a bulk

