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FERMI SURFACE AND dHvA EFFECT IN THE NORMAL STATE OF HIGH Tc A-15 SUPERCONDUCTORS


*Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.
†Department of Physics, University of Oregon, Eugene, OR 97405, U.S.A., and Physics Laboratory, University of Nijmegen, Nijmegen, The Netherlands
++Physics Laboratory, University of Nijmegen, Nijmegen, The Netherlands
+Mataplan Laboratory, University of Amsterdam, Amsterdam, The Netherlands
++Institute for Pure and Applied Sciences, University of California, San Diego, La Jolla, CA 92038, U.S.A.

Résumé.—La surface de Fermi de Nb₃Sn a été déterminée par des calculs de bande de type APW. Des oscillations de Haas-van Alphen (dHvA) ont été observées dans Nb₃Sn et dans V₃Si en accord avec la surface de Fermi calculée. Pour ces deux composés, à l'état normal les oscillations dHvA ont été observées avec des monocristaux ayant un haut rapport de résistivité plongés dans des champs magnétiques allant jusqu'à 400 kOe et les nouveaux détails de la surface de Fermi ont été mis en évidence et en particulier une structure ellipsoïdale osculatrice autour de M et une grande structure cubique autour de Γ.

Abstract.—The Fermi surface of Nb₃Sn has been derived from an APW band calculation. de Haas-van Alphen (dHvA) oscillations have been observed in Nb₃Sn and V₃Si which give a consistent FS description. Using single crystals of high resistance ratio's and magnetic fields up to 400 kOe, dHvA oscillations have been seen in the normal state for both specimens. New features of the Fermi surface include osculated ellipsoidal structure around M, and a large cubical structure around Γ.

The current high level of interest in A-15 materials is due to the recent continuing discoveries of the coexistence of a variety of anomalous normal state properties /1/ at both high and low temperatures, with the highest Tc 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 high transition temperatures observed in many A-15 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. Detailed knowledge of the band structure is a necessary precursor and underpinning to the inclusion of the electron-phonon and electron-electron couplings and hence to the theory of superconductivity in these materials. The only prior dHvA measurements on an A-15 are the recent results of Arko et al. /2/ for Nb₃Sb (Tc ~ 0.2 K). Magnetothermal oscillations were previously observed /3/ in V₃Ge (Tc ~ 6 K). Recently (some of us) have reported /4/ on the global energy structure of Nb₃Sn. Here we now report on band properties close to E_F = the derived Fermi surface. Briefly the calculated extremal cross-sectional areas agree within 3 to 5% with the dHvA data presented here for sheets near M. In addition we find a very large-massed (m* = 2.3) cubical "box-like" structure near Γ which we identify with breaks in the derivatives of the positron annihilation data of Samoilov and Weger /5/ on the isoelectronic material V₃Si.

Unfortunately, the very forces which make the high Tc A-15'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 for Nb₃Sb /2/. The four main limiting experimental factors are:

1) Cyclotron effective masses are expected to be high due to the intrinsically flat electronic band structure and to the strong electron-phonon coupling (λ = 1.4 for Nb₃Sn);
2) H_D is large, so that exceptionally high magnetic fields are needed, simply to reach the normal state;
3) Single crystals tend to grow nonstoichiometrically so that T_D, the Dingle temperature, would be expected to be large. The A-15's tendency toward intrinsic defect formation is presumably also accompanied by high dHvA Dingle temperatures;
4) Crystals undergo martensitic transformation in cooling from room to helium temperature, so that suppression of the dHvA signal due to interference of oscillations and to phase smearing between tetra-
gonally distorted subdomains is expected. Both phase smearing and scattering (Dingle temperature) contribute to an exponential attenuation of the dHvA amplitude, with phase smearing becoming more pronounced as the dHvA frequency increases.

The Nb$_3$Sn crystals were grown over a period of four months by closed tube vapor transport with iodine as the transporting agent. An inductive measurement of the actual dHvA crystal showed a $T_c$ 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. Assuming an approximate extrapolation function $\frac{1}{\beta}$ we estimate $R (300 K) / R (0 K) = 50$ and $R (0 K) = 1.5 \mu\Omega \cdot cm$. From this residual resistivity we estimate an electron mean free path of about 500 Å and $\omega_c \tau > 1$ in magnetic fields above 230 kOe, where $\omega_c$ is the cyclotron frequency and $\tau$ is a mean scattering time. This consideration is suggestive of the scattering time being high enough to see the dHvA effect.

The $V_3Si$ specimen was grown using a floating molten zone technique with induction heating in a pure argon atmosphere. The zone was passed along the rod (obtained by melting the consistent metals in a silver boat) at the rate of $\approx 2$ cm/h. A multi-grained sample was obtained which had a large central grain the length of the sample (1/8" diam.). No resistance ratio or $T_c$ measurements were made. However, it is known that $V_3Si$ is less susceptible than Nb$_3$Sn to the A-15 tendency toward defect formation, while the amplitude of the dHvA signals make it clear that the total scattering rate in $V_3Si$ must be at least comparable to that of Nb$_3$Sn. The quality of both the Nb$_3$Sn and $V_3Si$ crystals was very good, as indicated by examination of the room temperature diffraction spots in Laue back-reflection x-ray pictures. Both the Nb$_3$Sn and $V_3Si$ crystals were cut by spark erosion into specimens 2 mm$^3$ and surface damage etched away. Oriented single crystal samples were mounted in a spiral gear driven rotator with the magnetic field within about 1° of a (110) plane; the accuracy with which orientations are known in the (110) plane is also estimated to be about 1°.

The experiments were conducted at the University of Amsterdam's 400 kOe "slow pulsed field" facility using the magnet in the free inductive decay mode to minimize noise /8/. The output of a compensated dHvA pickup coil was differentiated twice, filtered to take out some of the dc voltage resulting from incomplete coil compensation, amplified and displayed directly on the recorder. A typical recorder tracing is shown in figure 1.

Fig. 1: Dual traces of a typical high speed chart recording for Nb$_3$Sn, showing the decay of a 40 T magnetic field pulse and the simultaneous recording of dHvA oscillations followed by the superconducting transition at $H_c^2$ versus time. The apparent oscillations below $H_c^2$ are noise generated in the pickup coil due to eddy currents, flux jumps, etc., and not periodic in $1/H$.

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. Beat structure, while obviously present at some orientations, was difficult to resolve because of the few oscillations. Nevertheless, it is possible to resolve several branches in the Nb$_3$Sn data. Figure 2 displays the dHvA frequencies (open circles) found for Nb$_3$Sn in the (110) plane, while the limited data for $V_3Si$ are given in Table I. The typical error estimates indicated in figure 2 are conservative, based on a maximum possible counting error of one-half oscillation.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Frequency ($10^8$ gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>6.24</td>
</tr>
<tr>
<td>[110]</td>
<td>4.60</td>
</tr>
<tr>
<td>[101]</td>
<td>7.78</td>
</tr>
</tbody>
</table>

Table I

<table>
<thead>
<tr>
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Until recently the intrinsic resolution of band theoretical calculations for materials as com-
plex as the A-15's was no better than about 4,000 K /1,9/ precluding direct theoretical exploration of electronically-driven models for the many interesting A-15 anomalies. However, we will interpret our experimental results here by comparing them with the Fermi surface predicted by a new high precision energy band model for Nb$_3$Sn, for which the intrinsic resolution is less than 500 K /4/.

Fig. 2: dHvA frequencies for Nb$_3$Sn in the (110) plane. The solid circles (and typical error bars) are the experimental results. Accuracy of orientation in the (110) plane is ±1°. The frequencies at a given orientation are reproducible to within a few %. The solid lines are generated from the Fermi surface model and band structure calculation of reference /4/.

In figure 3 we present the Fermi surface of Nb$_3$Sn (intersecting bands 15-21) in the principal symmetry planes. The Fermi energy was determined exactly from the density of states /4/ and no adjustable parameters were used. Because of the sensitivity of figure 3 to small energy shifts (especially bands 19 and 20) we have used the (larger than 300th order) APW secular matrix itself as an interpolation scheme to make the plot.

Two features are noteworthy compared to the previous V$_3$S$_4$ isolectric Fermi surface of Mattheiss /9/: 1) the greater confluence of osculated structure at M; 2) the flat "box-like" structures centered at Γ.

Globally the Nb$_3$Sn band structure was the same as that of Mattheiss. Making a microscopic comparison near $E_F$ between his /9/ figure 6(d) and figure 1 of reference /4/, we find that the main result is that $\Gamma_{12}$ has "dropped" by about 30 mRy relative sets of levels at M – a result easily understood in that we have included an extra (negative) potential inside the muffin-tin-spheres (primarily Nb-along-the-"chains") relative to Mattheiss. Hence the d-like Nb bonding state $\Gamma_{12}$ near $E_F$ – which is maximally sensitive to such effects - "drops" relative to the insensitive levels at M. Since the Fermi level follows the heavy massed $\Gamma_{12}$ state, the "light" massed M-centered hole-like levels seen in figure 3 "pop-up" through $E_F$. The structure near K also has a light mass. We have fitted the values of the "light-massed" bands 15-19 at 10 points near M to the lowest 7 M-harmonics by a least squares procedure:

$$E_n(k) = \Sigma c^n_{\text{imp}} x^y y^m z^p$$

where $E_n(k)$ is the energy of band n at point k, the $c^n_{\text{imp}}$ are the expansion coefficients and x, y, z are the components of the k-vector difference from M, in atomic units. All terms through quartic (i.e. $z^4$) were used. These were used to obtain the areas and masses, $m^* = (1/n)\Delta A/\Delta E$ listed in table II. In general, the correspondence between the observed and calculated dHvA frequencies (figure 2 and table II) is good. (The experimental labeling and identification was based on the angular dependence of the areas). We have listed in table II the masses for the M-centered pieces as a guide to understanding the experimental data. Very low dHvA frequencies we-
re discriminated against in the pulsed field experiments, both because their period in $H$ was too long and for other experimental reasons /10/. Most other M-centered "missing" orbits probably had too high a mass to be observed ($m^\text{exp}_{\text{band}}$ 2.4 $m^\text{theor}_{\text{band}}$), although it is surprising that $17(z)$ at [110] were missing. In view of the difficulty of the measurements and calculations the overall agreement is satisfactory and we conclude that the dHvA oscillations we have seen are consistent with a series of oscillated ellipsoids at M. Guided by Mattheiss' band calculations /9/, both Graebner and Kunzler /3/ (for $V_6O_6$) and Arko, Fisk and Mueller /2/ (for $Nb_3Sb$) have also interpreted their data in terms of M-centered structures, although those interpretations required rigid shifting of $E_F$ upward.

Table II
Areas and masses in the [001] and [110] directions in atomic units.
The convention of M labeling is as in figure 2.

<table>
<thead>
<tr>
<th>Direction</th>
<th>[001]</th>
<th>[110]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetry</td>
<td>A $m^\text{exp}_{\text{theory}}$</td>
</tr>
<tr>
<td></td>
<td>(x 100)</td>
<td>(x 100)</td>
</tr>
</tbody>
</table>

M-centered orbits

| 15(z) | 0.47 | 0.23 | 1.16 | 0.42 |
| 16(z) | 0.74 | 0.64 | 2.02 | 0.97 |
| 17(z) | 1.43 | 0.43 |     |     |
| 18(z) | 1.58 | 1.61 | 0.46 |     |
| 15(k,y) | 1.12 | 1.17 | 0.35 | 0.65 | 0.32 |
| 16(k,y) | 2.01 | 1.03 |     | 0.99 | 0.77 |
| 17(k,y) | 1.59 | 1.66 | 0.49 |     |     |

$\Gamma$-centered orbits

| 19 | 13.14 | 2.13 $\pm$ 0.05 | 13.66 | 2.90 $\pm$ 0.15 |

a) experimental data.
b) $m^\text{theory}$ should be multiplied by $(1 + \lambda) \approx 2.4$ to obtain experimental masses.

For the $\Gamma$-centered sheet, we have found it impossible to make a satisfactory expansion of the 19th band energy structure in a few cubic harmonics /11/, analogous to equation (1). The areas and masses listed in table II for the $\Gamma$-centered sheet were derived numerically from k vectors found from the APW secular matrix. The errors of the two 19th band masses are relatively large because they were found by numerical differentiation. (The effective energies used were spaced 0.5 mRy apart.) We have given M-centered and $\Gamma$-centered masses also to stimulate measurements of the cyclotron mass. The mass of the $\Gamma$-centered piece normal to [001] is rather constant for different values of $k_z$. Hence most of that Fermi surface sheet should contribute at a single value of $m^\ast$. This should help to make the rather high value of cyclotron mass of about 5 observable. Although our predicted Fermi surface is somewhat complicated, there are clear open and closed directions. We ask that high field magneto-resistance experiments be considered as a further test of our Fermi surface topology.

We now focus on an unexpected feature of figure 3: the two cubical "box-like" structures of band 20 and 19 centered at M and intersecting the $\Gamma$ to X ([100]) line at 0.15 and 0.64 $\pi/a$ units respectively, and the $\Gamma$ to $\bar{M}$ ([110]) line at 0.15 and 0.62 $\pi/a$ units, respectively. These features were invariant to slight shifts ($\pm 3$ mRy) of $E_F$, although the exact intersection distances varied slightly with $E_F$. Recently Samoilov and Weger have reported /5/ positron annihilation experiments in iso-electronic $V_6Si$ in the [001] direction, and we have enhanced the sensitivity of their data to Fermi surface effects by means of a novel "folding" technique. Although the resolution of their experiment was limited to 0.5 milliradians (or 0.196 $\pi/a$ units), they find (their figure 2) derivative structure with 3 peaks along [001] at 0.185, 0.635 and 0.844 $\pi/a$ units. Clearly there is good agreement between the flat band 20 and 19 intersections of [100] and their first two peaks. Band 20 is a possible candidate for their third peak structure -- particularly the flat structure centered around X in confluence with the multiple structure at M. But these third peak identifications are tentative. We have assumed an invariance between the detailed band structure shape near $E_F$ of $V_6Si$ and $Nb_3Sn$. Comparing figures 6a-6d of Mattheiss /9/ there is a close family resemblance -- but microscopically our $Nb_3Sn$ bands are more like his $V_6Si$ bands than his $Nb_5Sn$ bands. Samoilov and Weger have interpreted /5/ their data in terms of the independent band model /1/ whose chief difference near $E_F$ from our model is that they find that $E_F$ intersects the $\Gamma_{25}$, levels and that their $\Gamma_{18}$ levels are above $E_F$. Our results support Samoilov and Weger's main conclusion of the importance of planar Fermi surface structures along [100].
in A-15 materials although our interpretation and wave functions near $E_F$ is different from theirs. (If we artificially modify the potential to place $E_F$ at $\Gamma_{25'}$, we lose agreement with the M-centered dHvA data.) Weger has suggested [12] a high magnetic field NMR experiment as a definitive test of $\Gamma_{12}$ vs. $\Gamma_{25'}$ We ask that experimentalists also consider further high resolution positron annihilation work in A-15 materials along other high symmetry directions as a test of band models. We predict that there should be a smaller but similar break along [110] - we believe that the Samoilov-Weger model would predict smooth behavior in that direction.

The correspondence between the observed frequencies and those labeled 15(xy), 18n and 17(xy) is good. We conclude that the observed frequencies are consistent with a set of nested ellipsoids at M, similar to observations in Nb$_3$Sb [2] and V$_3$Ge [3]. The very low dHvA frequencies are discriminated against in pulsed field experiments, it is reasonable that we do not observe the lowest predicted branches of figure 2.

Finally, our present data clearly do not allow us to determine whether the disappearance of the higher frequency oscillations as a result of thermal cycling was due to the (progressive) disappearance of a piece of Fermi surface, accompanying the structural transformation, or simply due to an increase in Dingle temperature (electronic scattering rate) due to strain. 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. One would expect the degeneracy of the branches to be lifted, but our data are not sufficiently accurate to determine any minor splittings in the dHvA frequency branches. However, it does seem clear from our measurements that the effects of the martensitic transformation are reversible, and that it will be possible to use the dHvA effect as a detailed probe, in $k$-space, of the electronic consequences of the A-15 structural transformation.

We would like to acknowledge the help provided by Dr. Sven Hornfeldt in connection with the sample design, by Mr. Weizenbeek in connection with data logging, and the generous support provided to one of us (DHL) by the University of Nijmegen during the time these experiments were being conducted.

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