FERMI SURFACE MEASUREMENTS IN A-15 COMPOUNDS

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FERMI SURFACE MEASUREMENTS IN 4-15 COMPOUNDS

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The electronic structure of compounds based on the A-15 crystal structure continues to be the subject of intense investigation by theorists and experimentalists alike (Clogston and Jaccarino, 1961; Fisk and Webb, 1976; Hardy and Hulm, 1954; Matthias et al., 1954; Testardi, 1977; Weger and Goldberg, 1973). The basis for this is the widely held belief that the underlying electronic and/or phononic structure which is responsible for the unusual normal state properties is also connected with the occurrence of high T_c superconductivity (Testardi, 1977, and references therein) in this group of materials. This connection is illustrated by the structural distortion in V_3Si , which grows with decreasing temperature below the phase transformation at ~ 23 K, until it is suddenly arrested at T_c (Testardi et al., 1965; Batterman and Barrett, 1964; 1966). Like much of the A-15 behavior, the explanation of this effect depends on the interplay of many aspects of the problem; e.g., electrons, phonons, crystal structure and defects (Testardi, 1972; Varma et al., 1974). For such complicated systems, a clear picture of the basic electronic structure is essential to understanding the experimental behavior.

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All of the electronic structure models proposed to explain A-15 properties have stressed the importance of sharp structures near the Fermi level. In addition, various other features have been emphasized as being particularly relevant: narrow d-bands in the vicinity of E_F (Clogston and Jaccarino, 1961), the A-site one-dimensional interpenetrating chain structure (Iabbe and Friedel, 1966), flat planar pieces in the Fermi surface (Berko and Weger, 1972), and electronic instabilities at special points in the Brillouin zone which could drive the structural transformation (Abrikosov, 1975; Gorkov, 1974; Ho et al., 1979; Lee et al., 1977).

A number of band structure calculations have now appeared (Klein et al., 1978; Mattheiss, 1975; Pickett et al., 1979; van Kessel et al., 1978). High precision experimental studies of the k-space electronic structure in A-15's are required in order to evaluate the importance of these various models. The de Haas-van Alphen (dHvA) effect provides the most direct and highest precision method of Fermi surface determination presently known. Such measurements have now been carried out on a few A-15 materials (V_3Ge (Graebner and Kunzler, 1969), Nb_3Sn and V_3Si (Arko et al., 1978), Nb_3Sb (Arko et al., 1977)). Though not yet developed to the same degree as for pure metals (see, for example, Crabtree et al., 1979), these studies have already yielded valuable information. It is a difficult experiment in that good stoichiometric single crystals are difficult to obtain, and, in the case of high- T_c materials, magnetic fields $H > 20$ T are needed to reach the normal state (Foner and McNiff, 1976). This has precluded a thorough experimental examination in the first three materials where the strongest conclusion that could be made was that the observed surfaces are probably located at M. The situation is much better in the case of Nb_3Sb where crystals with resistance ratios 200-150 are available and the critical field is low. Because a complete detailed study of its Fermi surface can be done with present technology, Nb_3Sb can be used as a test case for evaluating different approaches to electronic structure calculations in A-15 materials.

In this paper we present new dHvA data in Nb_3Sb (now nearly complete) and compare them with the various band calculations, while at the same time reviewing the progress of Fermi surface measurements in A-15 compounds in general. Some definite statements can finally be made regarding the band structure. It appears that indeed the various theorists are converging on a more or less correct description in A-15 compounds, with those using a generalized potential having somewhat greater success than those making a muffin-tin sphere approximation.

II. REVIEW OF FERMI SURFACE DATA TO DATE

A. V_3Ge

This material was the first A-15 in which quantum oscillations (magnetothermal) were seen (Graebner and Kunzler, 1969). Three separate pieces of Fermi surface were observed which are consistent with cylindrical surfaces (possibly ellipsoids) centered at the M point in the Brillouin zone. Both the initial calculations of Mattheiss (1975) and subsequent work of Klein et al. (1978) predict structure at M as does the most recent calculation of Pickett et al. (1979) for isoelectronic Nb_3Ge . In all cases however, it appears that even the smallest predicted surface is at least twice as large as the smallest observed surface. Moreover, more structure is predicted than observed at M even though the expected effective masses (m^*), from a visual inspection of the bands, are not excessively high. It is difficult to carry the comparison further without either a set of predicted dHvA frequencies to compare with the data, or a more complete set of experimental frequencies. The theoretical Fermi surface is very complicated and possibly open in some directions. There is the additional complication of probable magnetic breakdown due to numerous degenerate bands which, we will see later, is very important in Nb_3Sb . What little experimental data exists is in qualitative agreement with theory, although no definitive statement can be made without a great deal more work. Using modern Fourier transform and field modulation techniques, much more can undoubtedly be learned about the V_3Ge Fermi surface.

B. Nb_3Sn and V_3Si

These data were obtained by direct inductive pickup of the magnetization utilizing the 40 T slow-pulsed magnet at the University of Amsterdam (Arko et al. 1978). The results of the Nb_3Sn investigation are shown as the data points in Fig. 1 superimposed on a background of frequencies predicted by van Kessel et al. (1978) and attributed to nested ellipsoids centered at M. Because the data are sparse, the apparent excellent agreement does not unambiguously confirm the band structure. Much more data will be needed for verification. (It might be pointed out that no adjustment of the calculation was needed to obtain this fit.) Only two orientations ([100] and [110]) were investigated in V_3Si with results nearly identical to those obtained in Nb_3Sn .

Further comparison of experiment and theory will be fruitless without experimental data on more of the Fermi surface. Especially in the case of Nb_3Sn , with its complex

Fermi surface and the magnetic breakdown that almost certainly occurs between nearly degenerate bands, a meaningful comparison would be very difficult. Perhaps the A-15 wars are better fought over a simpler material like Nb_3Sb , where a complete set of data is now becoming available.

III. RESULTS AND DISCUSSION OF Nb_3Sb

As already stated, a substantial amount of data for Nb_3Sb were first published (Arko et al., 1977) in 1977. Three pieces of Fermi surface were established on the basis of that data, the α , β and γ frequencies of Fig. 3. Only one family of frequencies (α) could be observed at all angles. In addition, fragments of the η and δ branches were observed but were too short to make any definitive statements. It was obvious that the rather complex Fermi surface would require a band structure to assist in identifying the experimental data.

Until very recently, no band structure calculation existed specifically for Nb_3Sb . Van Kessel et al. (1979), using the same technique as in their previous approach to Nb_3Sn (i.e. nonself-consistent APW, overlapping charge density model, but using extremely high precision) have now produced a set of bands complete with predictions of dHvA frequencies. This enormously simplifies comparison with experiment and allows quantitative rather than merely qualitative comparisons. Their predicted dHvA frequencies are shown in Fig. 2. The very close agreement between the α , β and γ frequencies and bands 18, 20 and 24, respectively, prompted us to re-examine Nb_3Sb in an effort to observe the missing bands 19, 21, 22 and 23, and the missing branches in band 20.

A complete new investigation was performed in the (100) plane utilizing the full power of the Fourier transform technique and the frequency discrimination capability of the field modulation technique. The new data was taken at slightly higher fields (to 75 kG) and lower temperature (0.35 K) than that already published. The experimental difficulties were enhanced by the complexity of the Fermi surface and the fact that amplitudes varied by several orders of magnitude even when the frequencies themselves were nearly identical. In addition, Fourier transforms of previous data were re-examined and found to confirm many of the new features we present here (new points in the (110) plane reported below were found in this way). Figure 3 contains the sum total of the frequency data obtained in Nb_3Sb .

A. High Frequencies $\approx 10 - 25 \times 10^6$ Gauss

Three unrelated sets of frequency branches have now been confirmed to exist (Fig. 3) above 10×10^6 Gauss. In keeping with our previous labeling, we call these γ , δ and η . If we compare this to Fig. 2, we find a great deal of correspondence even though the absolute values of the cross-sectional areas differ from predictions by as much as 20%. We can identify the γ frequencies with band 20, the δ frequency with band 21, and the η frequency with band 22. The γ -surface would then be an M-centered hole surface which is larger than predicted, while η and δ are R-centered electron surfaces, both smaller than predicted. A lowering of the Fermi energy by about 4 milliRydbergs would bring theory in line with experiment for these three surfaces, but, as we will see later, may cause problems for other pieces of the Fermi surface.

The γ_3 branch, previously observed only near [101] has now been found to connect with our previously labelled γ -frequency at [001] and the noncentral γ_2 branch connects with γ_3 as predicted by van Kessel et al. We have not observed the connection between γ_2 and χ and γ_1 , the signals in the region in question being just too weak. The splitting of γ_1 around [001] is easily understood as due to the slight, dumbbell shape of the band 20 surface (see Fig. 4) with γ_1 being the noncentral orbit.

The dashed-in portions of the δ and η frequencies in the (110) plane are done on the basis of the (100) plane observations and are meant only as an aid to the reader. We believe, however, that these will prove reasonably accurate when we examine the (110) plane in detail.

Theory fails to predict the multiple splitting of γ_1 near [110] in the (110) plane which may be due to magnetic breakdown involving band 19. Magnetic breakdown in fact is the most likely explanation for the very weak amplitudes of η , δ_1 , γ_3 and χ frequencies. The inset in Fig. 4 shows a plot of the predicted orbits for $H//[001]$. Note the large number of degeneracies where magnetic breakdown may occur on all surfaces except band 18. The effective masses [see van Kessel et al., this conference, for a detailed discussion of m^*] are in general not too large (max. $m^* = 1.7$ for band 21) so that one would normally not expect any of the amplitudes to be especially weak. Because of the weak signals and the dense bunching of frequencies, it is not possible to do an amplitude plot vs $1/H$ to look for breakdown effects in the usual manner. We would point out, however, that the η frequency increased in amplitude by one order of magnitude as we tipped H from [101] by a mere 5° . In this angular range the number of possible breakdown switching junctions would have decreased from 8 to

2 for η . Furthermore, at both [100] and [101] we observe numerous additional Fourier peaks in the transform (see Fig. 4) which we cannot follow for more than $\sim 5^\circ$. Some of the stronger peaks have been included as circled data in Fig. 3. We believe these are magnetic breakdown orbits.

In general, there is excellent topological correspondence and rough quantitative agreement between theory and experiment for the higher frequencies.

B. Low Frequencies $< 5 \times 10^6$ Gauss

The picture is somewhat less neat and tidy at lower frequencies. It is not a lack of Fourier transform peaks that creates the problem, but rather their profusion. The problem arises from the low masses of frequency branches α_1 ($\approx 0.3 m_0$) which result in numerous harmonics which often tend to obscure real data. There may also be some confusion due to magnetic breakdown. Figure 3 shows the data which we cannot account for as being due to harmonics of α_1 except for the circles which we include for reasons stated later.

A comparison of Fig. 3 with Fig. 2 shows that frequency β can be identified with the band 24 surface and frequency μ with the band 23 surface. Both of these are R-centered electron surfaces and the agreement between theory and experiment is better than 2%. Thus, a lowering of the Fermi energy can only make matters worse for these R-centered pieces.

A similar phenomenally good agreement is found for the frequency branches α which would seem to correspond to band 18, an M-centered hole ellipsoid. There are, however, several problems in the comparison. The theory of van Kessel et al. predicts a second M-centered hole ellipsoid from band 19 which we are not certain that we have observed. The reason for the uncertainty is that while we do observe a very weak frequency branch (ζ_1 in Fig. 3) that cannot be accounted for as being due to harmonics of α_1 , and which is approximately of the correct cross-sectional area to correspond to the lower branch of the band 19 ellipsoid, the middle branch of band 19, ξ_2 , falls precisely on the second harmonic of α_2 ($= 2\alpha_2$) and may not be distinguishable as an independent frequency. Moreover, the upper branch of band 19 is not observed. It can be argued that this is due to magnetic breakdown since band 19 is degenerate with band 20 along the R-M line thus affecting the upper branch in the entire (100) plane. We find amplitude of the $2\alpha_2$ branch to be considerably larger than $2\alpha_1$ or $2\alpha_3$, indicating there may indeed be a separate orbit at this frequency. (These are the circles in Fig. 3). This question is yet to be resolved.

Another unexplained feature is a weak frequency (ν) at $\approx 0.4 \times 10^6$ Gauss. This very small frequency cannot be optimized with our apparatus and hence cannot be mapped out in detail. We know that it does not have the symmetry of Γ or R since multiple frequencies are observed. It appears to have a heavier m^* than the α_i frequencies. A preliminary magnetoresistance experiment yielded quantum oscillations of this frequency. Thus ν is possibly a switching orbit controlling magnetic breakdown, but the small signals and the low frequencies again do not allow a detailed mapping. It is also possible that by lowering the Fermi energy 3-4 mRy we obtain an additional piece of Fermi surface either from band 20 along the Q-M line or from band 17 along the R-M line.

IV. DISCUSSION AND CONCLUSIONS

We have seen that there is not only qualitative but also a great deal of quantitative agreement between experiment and the band structure calculation of van Kessel et al. Very small pieces of Fermi surface are always difficult to determine in any calculation so it is gratifying to see that the problems occur with these pieces. It must also be emphasized that the bulk of bands 21, 22, 23 and 24 were discovered only after being predicted by van Kessel et al., as well as some rather crucial connections on band 20.

We have confined our comparisons of the data to the calculations of van Kessel et al., primarily because their theoretical dHvA frequencies (Fig. 2) allow quantitative comparison. But we can also make qualitative comparisons with other calculations.

There are two other preliminary, unpublished calculations for Nb_3Sb , one using the LMT0 method (Jarlborg, private communication) with no nonspherical corrections and the other using self-consistent APW again with no inside muffin-tin corrections (Klein, private communication). In both cases a correct description is obtained around the R-point, but shifts of ≈ 30 mRy at the M point are needed to obtain the small hole pockets.

One can also gain some insight by using a rigid band shift of Nb_3Sn or Nb_3Ge bands to correspond to Nb_3Sb . Since the wave function character at E_F is primarily d-like and coming from Nb sites, a rigid band shift can be useful if one recognizes that results are only qualitative. Using such a shift for the Nb_3Sn bands of van Kessel et al. (1978) and Nb_3Ge bands of Pickett et al. (1979) we obtain a qualitatively correct description at both M and R while a similar shift of the corresponding bands of Klein et al., (1978) results in a

correct description at R but approximately the same 30 mRy failure at M. The calculations of van Kessel et al. and Pickett et al. both use a generalized potential and their resulting bands are strikingly similar.

It is curious that nonspherical corrections inside the muffin-tin sphere should result primarily in an upward shift of some bands at the M point. Perhaps there is some important physics to be learned from this. We ask our theoretical friends to clarify this point.

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FIGURE CAPTIONS

FIGURE 1. H/gH data (circles) superimposed on a plot of predicted dihh frequencies (solid lines) for H/gH (1979). The numbers (1b, 2a, ...) refer to the predicted dihh labels (level 1b, $\pi/2$, $\pi/2$, ...) which contain).

FIGURE 2. Predicted dihh frequencies for H/gH for H/gH (1979), et al. this conference.

FIGURE 3. Experimental dihh frequency spectrum for H/gH . Peaks in (110) plane are noted to show the experimental resolution.

FIGURE 4. Fourier transform of dihh data for H/gH (1979). Lower frequencies ($0-10 \times 10^6$ Gauss) are shown in the 1st trace, with frequencies below 2.9×10^6 Gauss magnified $\times 10$. Upper trace shows frequencies above 10^7 Gauss. All unidentified peaks are observed only near the symmetry axis and are probably a result of magnetic breakdown. Inset shows the H - and H -centered orbits for $H/(001)$ from van Housen et al., this conference. It is the magnetic regeneration.

Fig. 1

Fig. 2

MAGNETIC FIELD DIRECTION

Fig. 4