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by

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1. Introduction

The properties of metals can be roughly but usefully divided into two groups: one-electron effects which depend mainly on the interaction of conduction electrons with the periodic crystal potential, and many body effects for which interactions of the electrons with each other or with vibrations of the lattice are required. One-electron properties can be calculated within the framework of band theory and have a long history of theoretical investigation with a wide variety of models. Cohesive energy, structure type, lattice constant and bulk modulus can all be understood in this way. Fermi surface geometry has received a great deal of attention because it is a central result of band theory that can be directly verified by experiment. The band density of states is also a key result giving the one electron contribution to the electronic specific heat and Pauli susceptibility, though these quantities are enhanced by many body effects as well.

The many body interactions are less well understood theoretically even though they are responsible for the most interesting metallic behavior. Much attention has been focussed on the electron-phonon interaction in the last decade or so with the goal of predicting the occurrence of superconductivity and explaining the temperature dependent resistivity of metals. Equally important are the exchange interaction and paramagnon effects which give rise to large magnetic susceptibilities and spontaneous magnetism. These problems are difficult to treat in a true many body sense, though much progress has been made in calculating magnetic properties in a one-electron framework using the mean field approximations of local spin density theory.

In the pure transition elements our understanding of one-electron properties is fairly well established. Band theory calculations and Fermi surface measurements have been done for most of the series. Usually Fermi surface topology is predicted exactly and quantitative geometrical features to better than 10%. The greatest current interest in the elements centers on the many body problems: magnetic effects arising from exchange and correlation and the superconducting properties due to electron-phonon interactions. The energies and wave functions of band theory play a central role in treatments of these many body effects. It is because the one-electron properties are so well established that the many body effects can be addressed.

For metallic compounds our understanding is not so far advanced. There is not a large storehouse of theoretical and experimental data available for comparison. Models of one electron behavior and the role played by specific features (e.g. charge transfer between constituents,

muffin tin approximations, exchange and correlation in narrow band compounds, importance of self-consistency) have not been extensively analyzed. Without reliable one-electron information it is difficult to treat the many body effects. Experimentally, intermetallic compounds are difficult to study because crystal preparation problems are often severe. Phase transitions as a function of temperature or composition, slight deviations from stoichiometry and the occurrence of structural defects often prevent the growth of high quality crystals needed for Fermi surface work.

In this review we describe how Fermi surface properties measured by the de Haas-van Alphen (dHvA) effect can be used to study one-electron and many body effects in elements and intermetallic compounds. In both cases two experimental advances play a crucial role: the use of high magnetic fields and the development of fast convenient Fourier transform spectroscopy. High fields are required because the metals which show interesting superconducting and magnetic properties are those with a high density of states and large cyclotron masses m*. The exponential reduction in dHvA signal caused by these large masses can best be minimized by application of high fields. Poor quality crystals further reduce the signal, making high fields even more important for studying intermetallic compounds. In this regard our current field of 15 T is nowhere near the useful upper limit. There are many compounds that will require fields double or triple this value to obtain a reasonable picture of their Fermi surface properties.

Fourier transform capability is essential to sort out the many separate frequencies in dHvA spectra of metals with complex Fermi surfaces. While this capability has existed in principle for many years, it is only with the advent of inexpensive laboratory computers that the experimenter has had immediate, convenient access to the Fourier transform information at the same time the data is recorded. This tremendously simplifies the logistics of the experiment, allowing the most important and useful data to be identified and studied quickly and efficiently.

The dHvA effect gives three kinds of basic orbital information: extremal cross sectional area, cyclotron effective mass, and conduction electron g-factor. The measured orbital g-factors give precise information about the Zeeman splitting of the conduction electrons and in principle can be used to study exchange enhancement of the conduction electron susceptibility and the transition to ferromagnetism. This field is not well developed, mainly because theorists have not yet addressed the problem of predicting one-electron g-factors from band theory. Revealing experiments have been done in several transition elements (Hornfeldt et al 1969, 1976), and there is potential for much more work in this somewhat neglected area.

Of the remaining two quantities, the cross sectional area gives precise Fermi surface geometry and is a one-electron property directly predicted by band theory. The cyclotron mass has one-electron contributions related to the slope of the energy bands at the Fermi level and many body contributions coming from the electron-phonon and electron-electron interactions. To study the many body effects the one-electron contribution obtained from a suitably verified band structure must be

subtracted off. In the elements, where band theory predicts Fermi surfaces in good agreement with experiments, this subtraction can be done with reasonable confidence while in compounds the generally poorer agreement between theory and experiment leaves more doubt about its validity.

2. Transition Elements

The most useful tools for interpreting the detailed orbital areas and masses obtained from dHvA experiments on transition metals are the parametrization schemes. The object of these schemes is the conversion of orbital information into "point" or local k-dependent quantities. These point quantities when properly averaged over a cyclotron orbit give the measured orbital quantities; if averaged over the Fermi surface, they give a bulk property which can be measured in another experiment or is otherwise known. For cross sectional areas the point quantity is the Fermi radius vector $\vec{k}_F$, and the surface averaged quantity is the volume of the Fermi surface which is proportional to the number of conduction electrons per atom. For cyclotron masses, the point quantity is the Fermi velocity $\vec{v}_F$ and the surface averaged quantity is the density of states at the Fermi level, which is proportional to the electronic specific heat.

The great advantage of these schemes is that they convert the measured orbital quantites to much more useful forms. Point properties give the most detailed comparison with theory, which deals naturally with individual $\vec{k}$-states. Indeed, because modern band theory predicts elemental Fermi surfaces so well, comparisons at the k-vector level are very useful for studying the small remaining discrepancies. Subtraction of the band contribution from the parametrized Fermi velocities allows the detailed k-dependence of the many body renormalization to be derived. This is the only technique currently available for deriving the anisotropy of many body effects over the Fermi surface.

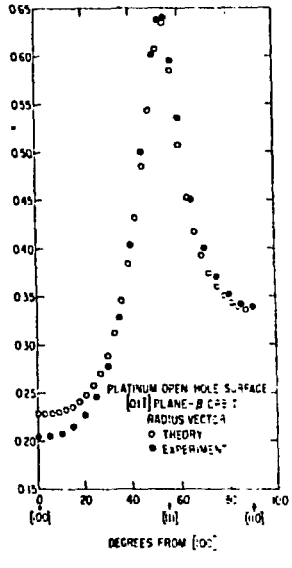

Figure 1: Fermi radius vector measured from the X point for the (01$\bar{1}$) plane of the open hole surface of Pt. Solid circles are the KKR parametrization of Dye et al (1978), open circles the band calculation of Watson-Yang et al (1977). The ordinate gives the radius vector in atomic units. On the abscissa, [100] is along X-Γ, [111] is along X-L, and [110] is along X-U.

The most powerful parametrization schemes for transition elements are based on the KKR method of band calculation (Crabtree et al 1979a and references therein). Using the KKR phase shifts evaluated at the Fermi energy as adjustable parameters, the detailed Fermi surface geometry can be recovered from the measured cross sectional areas. In a similar way, the energy derivatives of the KKR phase shifts may be adjusted to fit the cyclotron orbital masses and recover the detailed k-dependence of the Fermi velocity. The remarkable feature of these schemes is that so few parameters are required to fit the Fermi surfaces so accurately: for the noble metals three parameters are enough (Shaw et al 1972), for the three sheets of the Nb surface five phase shifts are required (Crabtree et al 1979b), and for Pt (Dye et al 1978) and Pd (Dye et al to be published) with three and four sheets, respectively, no more than seven parameters are needed.

The ability of these schemes to accurately represent Fermi surface properties can be judged on three levels: comparison of point properties with band theory, comparison of orbital properties with those measured, and comparison of surface averaged properties with specific heat experiments and requirements of charge neutrality. Figure 1 shows a comparison of the Fermi radius vector in the $(01\bar{1})$ plane for the open hole surface of Pt as given by the KKR parameterization (Dye et al 1978) and the non-self-consistent, overlapping charge density, warped muffin tin band calculation of Watson-Yang et al (1977). The excellent detailed agreement is typical of results for transition metals and shows that both the parametrization scheme and the band structure describe the Fermi surface essentially correctly. For careful band calculations in which the mathematical and physical approximations are controlled, the small remaining differences reflect inadequacies in the physical assumptions of the band model (Elyashar and Koelling 1977). In these cases detailed comparison of the k-vectors is the most useful way to study the discrepancies.

The quality of the orbital data produced by the parametrization schemes is demonstrated in Figure 2, which shows the angular variation of cross sectional area for the β and γ orbits on the open hole surface of Pd (Dye et al, to be published). The β orbit is centered at the X point

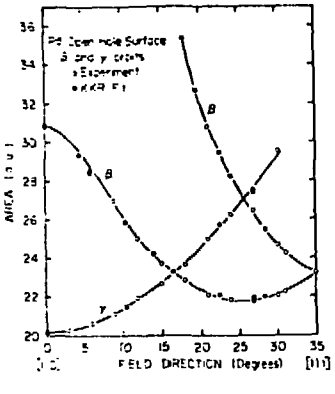

Figure 2: Extremal orbital areas as a function of field direction for the β and γ orbits in the (110) plane on the open hole surface of Pd (Dye et al to be published).

of the Brillouin zone and has two branches for fields near [111], while the γ orbit is a non-central orbit located near β. Both orbits probe a

highly distorted region of the Fermi surface strongly affected by a van Hove singularity (Anderson 1970). The close agreement between parametrization and experiment is especially convincing for the γ orbit because its center is not restricted to a high symmetry point but changes with field direction according to the extremal area condition. To reproduce the area of such an orbit so well over an angular range of 30° indicates that even the finest details of the Fermi surface are very well represented.

At the surface average level, the parametrization schemes can be checked by two quantities. Charge neutrality requires a certain integer number of conduction electrons per atom, which fixes the volume contained in the Fermi surface. Electronic specific heat experiments measure the enhanced density of states, which is proportional to an integral of the inverse Fermi velocity over the Fermi surface. Both the volume and density of states integrals can be done in a straightforward way using the point radii and velocities of the parametrization scheme. The results are shown in Table I for Nb, Pt, and Pd. In all

Table I. Fermi surface average quantities calculated from KKR paramatrizations. Fermi surface volumes are given as volume of electron sheets - volume of hole sheets. Experimental specific heat data are taken from Ferreira da Silva et al (1969) for Nb, Dixon et al (1965) for Pt, Boerstal et al (1971) for Pd.

	Volume of Fermi Surface Brillouin Units		Enhanced Density of States states/eV-atom-spin	
	KKR	Charge Neutrality	KKR	Specific Heat
Nb	-1.0034	-1	1.68	1.66
Pt	.00413	0	1.37	1.38
Pd	.00381	0	1.74	2.00

three metals charge neutrality is satisfied to a very high degree. Except for Pd, which we discuss below, the enhanced density of states determined from the fit agrees very well with specific heat results. From the examples given here and from detailed results presented elsewhere, we see that the parametrization schemes give a very detailed and consistent picture of transition metal Fermi surface properties.

With such a detailed model, we can study anisotropy in the many body effects. For Nb, with the highest superconducting T_c (9.25 K) among the elements, the dominant many body effect is the electron-phonon interaction (although the electron-electron and paramagron effects may not be negligible). The strength of the interaction $\lambda(k)$ for particular k states can be obtained from the ratio of band and experimental velocities (Crabtree et al 1979b)

$$1 + \lambda(\vec{k}) = \frac{|\vec{v}_b(\vec{k})|}{|\vec{v}_{exp}(\vec{k})|}$$

When properly averaged over the Fermi surface $\lambda(\vec{k})$ gives an average value which should be compared with those determined from comparing experimental and band density of states or by inverting empirical McMillan-like equations. Results for $|\vec{v}_b|$, $|\vec{v}_{exp}|$, and $\lambda(\vec{k})$ for Nb are shown in Figure 3, where the band velocities are taken from the relativistic, self-consistent general potential calculation of Elyashar and Koelling (1977). (The p states in their calculation were lowered by 50 mRyd to remove a slight disagreement with the experimental Fermi surface).

From the variation of $\lambda(\vec{k})$ over the Fermi surface, one can also derive information about the variation of the superconducting energy gap $\Delta(\vec{k})$ (Crabtree et al 1980). Both of these quantities play central roles in current theoretical efforts to calculate superconducting properties from first principles (Butler et al 1979,

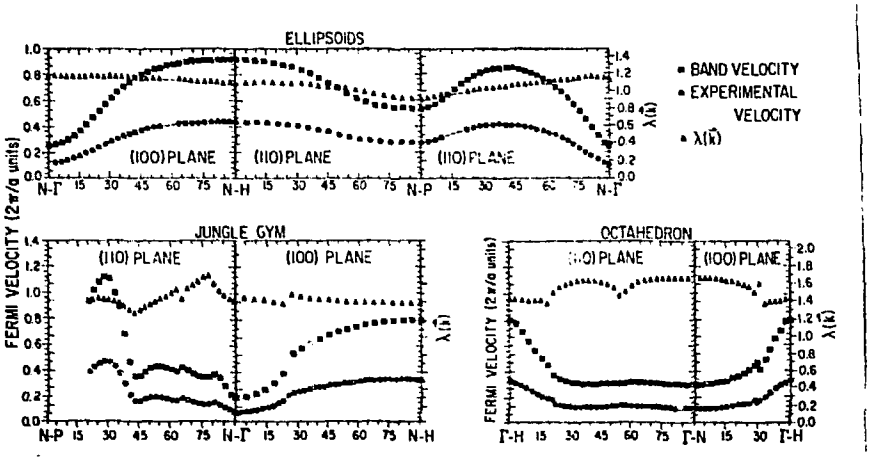

Figure 3: Comparison of band and KKR parametrized Fermi velocities from dHvA experiments for the symmetry planes of the Fermi surface of Nb. The derived values of $\lambda(k)$ are also shown, to be read from the right hand ordinate.

Peter et al 1977, Harmon and Sinha 1977, Varma et al 1979). The anisotropy in these quantities provides a much more detailed and useful test of theory than can be obtained from the single surface averaged quantity λ or Δ usually obtained in other experiments. The reason is that the final theoretical value for the surface averaged quantities depends on an overall normalization for the strength of the interaction, which is difficult to calculate from first principles. With anisotropy information, trends in the point by point variation over the Fermi surface can be compared without the need for this normalization.

In Pd, both electron-phonon and many electron effects are important. From trends across the transition series (Butler 1977, Papaconstantopoulos 1977, Pinski et al 1978) one expects an electron-phonon interaction strength of $0.2 < \lambda < 0.4$, strong enough to produce superconductivity. The tendency to superconductivity is opposed by electron-electron and paramagnon effects, which favor magnetism and produce a highly exchange enhanced susceptibility. Judging by the total enhancement in the measured specific heat (Boerstal et al 1971) over the bare band value (Anderson, 1970, MacDonald et al, unpublished) electron-electron and electron-phonon contributions are about equal.

The most striking feature of our results on Pd is that the enhanced density of states predicted by our fit is 13% lower than the value given by specific heat experiments. We do not believe this is due to failure of the parametrization scheme, as the same techniques work quite well for Pt (Dye et al 1978) which has very similar Fermi surface properties. The disagreement is totally unexpected, since conventional wisdom holds that the enhancement effects operating on the specific heat and cyclotron mass are not observably different. An especially intriguing possibility is that we are seeing magnetic field inhibition of the paramagnon enhancement to the cyclotron masses, which were measured in fields up to 120 kG. If so, the effect is much larger than expected, though estimates its magnitude are usually based on oversimplified models of the electronic structure of Pd (Brinkman and Englesberg 1968, de Chatel and Wohlfarth 1973). Far more theoretical effort is required in this area if we are to understand the physics of narrow band metals, of which Pd is the most outstanding and the best studied example in the transition series.

3. Intermetallic Compounds

Intermetallic compounds show a much greater variety of physical behavior than the transition metals. The compounds tend to fall into classes typified by specific properties. Examples are high T_c superconductors in the A15 structures, local moment metals in rare earth and some actinide compounds, mixed valence metals among compounds of Ce and Yb, itinerant magnetism in certain C15 Laves phases, and superconducting-magnetic phase transitions in ternary superconductors. All of this behavior depends in a fundamental way on conduction electron properties and requires for its explanation knowledge of the electronic structure. Because there is relatively little experimental information available, the greatest need at present is to carry out as thorough Fermi surface measurements as possible in compounds which are prototypical of a particular class.

A good example of this approach is the recent work on Nb_3Sb, an A15 superconductor (Arko et al 1980). The high T_c's in these materials may depend on a variety of special features like the chain-like structure of the transition metal atoms and the occurrence of defects and phase transitions in the lattice, as well as the basic electronic and phononic structure. To form a clear picture of the A15 electronic structure, a careful comparison of experiment with several band calculations based on different models is required. Nb_3Sb is one of the few A15's which can serve as a good representative: high quality stoichiometric crystals are available, it has a low critical field allowing the field penetration required for Fermi surface work, its

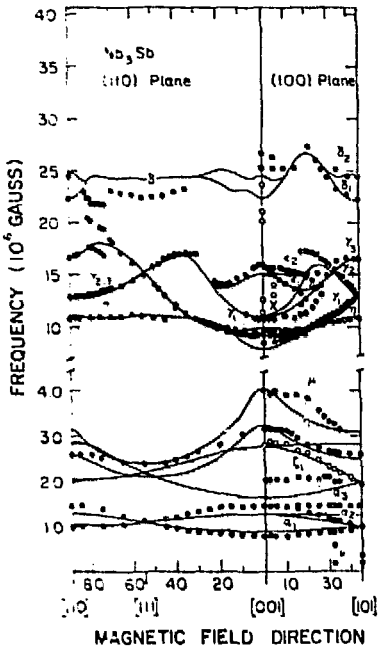

Figure 4: Experimental Fermi surface areas as a function of field direction for the A15 material Nb_3Sb. Solid lines are the band calculation of van Kessel et al (1980), shifted slightly to show the correspondence.

effective masses are low enough so that all of the Fermi surface can be observed, and it is closely related to the high T_c material Nb_3Sn since Sb and Sn are in neighboring columns but the same row of the periodic table.

The experimental data for the Fermi surface geometry are shown in Figure 4 along with the predictions of band theory due to van Kessel et al (1980). The theoretical areas have been shifted slightly to make the correspondence more obvious. It can be concluded from the complexity of the experimental data and its very good qualitative agreement with the band theory that the basic approach of the calculation is correct. This is in contrast to calculations which do not allow for non-spherical charge distributions around the Nb site (Jarlborg, private communication, Klein, private communication). In these cases the band structure around the M point in the Brillouin zone is found to be shifted by about 30 mRyd, leading to qualitatively incorrect predictions for the affected sheets of the surface.

The mixed valence metals form another class of compounds for which experimental Fermi surface information is needed. Here the electronic and lattice properties are strongly affected by the f-electrons, which occupy states intermediate in character between local and conduction states. Often the apparent valence of the f atom changes, either continuously or suddenly, with temperature, pressure, or alloy concentration. In various theoretical models the mixed valence effects depend on quantities like the width of the f levels, their position relative to the Fermi level, and the amount of hybridization between f and conduction states. To date the field has lacked the kind of incisive experiments that can look at these quantities directly, relying instead on probes of the local environment like Mössbauer effect and XPS or on general macroscopic probes like susceptibility and resistivity.

In order to explore the conduction electron properties of mixed valence systems we have begun dHvA studies of $CeSn_3$ (Johanson et al 1980a) a metal whose valence properties evolve continuously with temperature. Our data show as many as nine separate extremal areas for some field directions, and effective masses ranging from 0.3 to over 9 for some of the larger areas. These very high masses indicate the existance of flat energy bands as would be expected from hybridization with the 4f levels of Ce. As a reference metal we are also studying $LaSn_3$ (Johanson et al 1980b) which has similar electronic properties but without the mixed valence effects associated with the f electrons. Further details of this work will be reported in later publications.

4. Conclusion

The examples given above demonstrate the power and versatility of the dHvA effect in studying electronic behavior in metals. In transition metals the parametrization schemes give a very complete and consistent picture of the k-dependent and surface averaged electronic properties. Because the one-electron behavior is fairly well known, the many body contribution to the Fermi velocity can be isolated and its detailed anisotropy can be displayed. This kind of information is directly relevant to the calculation of electron-phonon interaction effects and cannot be derived by any other means.

Intermetallic compounds offer a much greater range of interesting many body phenomena combined with a generally lower level of theoretical understanding. In many cases the basic one-electron features have not been measured, and this area has great potential for future growth. As the one electron aspects become better understood the many body information in the measured effective masses also may be more fully exploited. Experimentally the field is limited by the availability of good crystals and high magnetic fields. As these limits are pushed back, we can expect the dHvA effect to continue supplying the high quality detailed information about Fermi surface electrons that is needed for a basic understanding of metallic behavior.

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