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INVESTIGATION OF ELECTRON LIFETIMES IN MOLYBDENUM
WITH DILUTE SUBSTITUTIONAL IMPURITIES*

by

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Investigation of Electron Lifetimes in Molybdenum with Dilute Substitutional Impurities*

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I. Introduction

Recently Springford has reviewed¹ the anisotropy of conduction electron scattering in the noble metals. Since the de Haas-van Alphen effect yields a narrow orbital scattering rate, rather than an average over the entire Fermi surface, as is true in resistivity, a systematic set of measurement holds out the promise of providing a detailed set of local scattering rates or lifetimes. Indeed Springford emphasizes this possibility by denoting such techniques as direct methods.

In this paper we examine the effect of a series of dilute transition and actinide impurities on the electronic lifetimes in the host molybdenum. The Fermi surface and electronic structure of molybdenum have been studied by a number of workers.^{2,3} Although the specific heat is small,³ the d- probability at the Fermi energy is large,⁴ making molybdenum an excellent host to study the effect of transition metal impurities in a transition metal host using the de Haas-van Alphen effect.

In order to make best use of these data it is necessary to invert⁵ to find local or point scattering rates. We have developed⁶ a new and simple scheme for centro-symmetric sheets, which we present in detail in the present paper. We also consider the important relationships between the errors in the orbital scattering rates and the errors in the derived point scattering rates, since for a constant orbital error, the point error is not constant.

The plan of this paper is as follows: Section II gives the experimental details, Section III the inversion scheme, the results are discussed in Section IV and our conclusions are drawn.

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II. EXPERIMENTAL

a) Sample Preparation

Starting material with a residual resistance ratio of ~ 2000 was drilled the length of the rod, cleaned, and welded at one end. Impurities were introduced in the form of wire or chips into the center of the molybdenum rod in the desired concentrations and the combination zone-refined twice. The final concentrations were determined in various ways. Tungsten impurity concentrations were initially obtained to $\pm 10\%$ using spectrographic analysis. Subsequent concentrations were obtained from resistance ratio measurements. The concentrations of the samples used can be obtained from Fig. 3. Uranium and ruthenium both have relatively low vapor pressures, thus it was assumed that no material was lost in zone refining so that the final concentrations equalled the starting concentrations. The error bars were obtained from the variation of the resistance ratio across the specimen. Because of the high vapor pressure of Fe at 3000°K it was necessary to start with a mixture containing up to 2 at. % Fe and to make the zone pass at ~ 10 mm/min in order to obtain a single crystal specimen having about 20 P.P.M. Fe. The concentration was determined from a measurement of the susceptibility vs. temperature, determining the Curie constant C and assuming $^7 P_{\text{eff}} = 3.0 \mu_B$.

The single crystal alloys were sliced into 1 mm thick discs and electro-etched to reveal sub-grain boundaries and dislocation etch pits.⁸ Samples with final dimensions of ~ 0.5 mm on a side were cut from sub-grain free regions having the smallest dislocation density. These techniques substantially reduced phase smearing due to inhomogeneities in the specimens. Orbital Dingle temperatures for several equivalent crystallographic (off-axis) directions generally reproduced to better than 0.1°K .

b) Measurement

A rotating probe capable of two degrees of freedom was used to orient the sample in the magnetic field. Samples were thus oriented by means of the dH ν A effect itself. Problems of backlash are greatly reduced by always rotating or tilting in the same direction; nevertheless, there is a residual uncertainty

of about $\pm 0.5^\circ$ in the orientation. Since one must be oriented⁹ to within $\approx 0.05^\circ$ of the axis to avoid phase smearing due to sample inhomogeneities one understands the extra precautions needed in sample preparation to reduce such smearing.

Direct measurement by means of a magnetoresistance probe was used to map magnetic field inhomogeneities.¹⁰ It was determined that in the volume occupied by the specimens the field inhomogeneity was 3-5 PPM.

The hole octahedron centered at H was studied in Mo(W), Mo(Ru) and Mo(Fe) alloys (See Refs. 2 or 3 for the Fermi surface of Mo). Since the octahedron frequency is well above the ellipsoid and lens frequencies (the jack frequencies are generally quite weak, appearing only as beats on the octahedron frequency) a single frequency could be selected in the dHvA spectrum and the data could be analyzed without the aid of a computer. In order to measure the Dingle temperature on the remaining sheets of the Fermi Surface, an on-line PDP-11/20 mini-computer was utilized. Data were taken in equal length blocks between 30 and 65 kG with each block containing a sufficient number of oscillations to avoid overlapping of peaks in the Fourier transform. A complete study was done on the Mo(U) system only.

The need for accurate effective mass measurements soon became apparent in our work, necessitating the installation of an insert dewar. (Our original data on Mo(W) were taken at 1.9°K with no insert dewar.) Masses were measured to within 2% between 2.0°K and 1.1°K at fields low enough to avoid magnetic interaction effects. For the alloy samples studied, this was usually less than 50 kG.

11. Inversion Scheme

1) Formalism

As has been stressed before⁶ one of the great advantages of measuring scattering probabilities by means of the dH VA technique is that for a sufficiently simple sheet of the Fermi surface, the orbitally averaged scattering rates may be inverted to yield unique point scattering rates. The motivation for such a procedure, although difficult to actually carry out in practice, is two-fold: (1) The symmetry and consistency of the data are tested in a severe way; (2) The inversions are carried out using a model based solely on the experimental symmetry of the data and not, for example, on the assumption that the impurity has a potential which is representable by a particular form (suffin-tin, for example). This motivation has produced a number of inversion schemes; the only advantage of ours is extreme simplicity.

The basic equation for the orbital lifetime τ_{orb} has been given by Lowndes⁵

$$\frac{1}{\tau_{\text{orb}}} = \frac{1}{T} \int_0^T \frac{1}{\tau(\vec{k})} dt(\vec{k}), \quad (1)$$

where the period $T = 2\pi/\omega_c$, the cyclotron frequency $\omega_c = \frac{eH}{m^*c}$, and m^* is the orbital mass. Let us define the orbital Dingle temperature $T_{\text{orb}} = \pi/(2\pi K \tau_{\text{orb}})$ and the point Dingle temperature $T_{\text{pt}}(\vec{k}) \equiv \pi/[2\pi K \tau(\vec{k})]$, where K is Boltzman const. Then (1) becomes

$$\frac{2\pi m^* c}{eH} T_{\text{orb}} = \int_0^T T_{\text{pt}}(\vec{k}) dt(\vec{k}), \quad (2)$$

where again, the particular orbital path of $\vec{k}$ is chosen by the left hand side of (1). From the Lorentz relation, $d\vec{k}/dt = e\vec{v} \times \vec{H}/\hbar c$, and converting to path length variable $d\vec{k}$, we obtain

$$dt(\vec{k}) = \frac{\hbar c}{eH} \frac{d\vec{k}}{v_{\perp}} \quad (3)$$

where $v_{\perp}$ is the component of $\vec{v}$ in the plane normal to $\vec{H}$ at the point $\vec{k}$.

Then (2) becomes:

$$m^*(\hat{\epsilon}) T_{\text{orb}}(\hat{\epsilon}) = \frac{\hbar}{2\pi} \oint d\vec{k} T_{\text{pt}}(\vec{k})/v_{\perp}(\vec{k}), \quad (4)$$

where the path of $d\vec{k}$ has been chosen by the magnetic field direction $\vec{H}$, and $\hat{\epsilon}$ is a unit vector in the direction of $\vec{H}$. We can gain insight into (4) by the equation for the orbital area¹¹

$$A(\hat{\epsilon}) = \frac{1}{2} \oint \rho^2(\hat{\xi}) \delta(\hat{\xi} \cdot \hat{\epsilon}) d\Omega(\hat{\xi}) \quad (5)$$

and the related one for the orbital mass $m^*(\hat{\epsilon})$

$$m^*(\hat{\epsilon}) = \frac{\hbar^2}{2\pi} \oint \frac{\rho(\hat{\xi}) \delta(\hat{\epsilon} \cdot \hat{\xi}) \Omega(\hat{\xi})}{h v_{\perp}(\hat{\xi})} \quad (6)$$

which is obtained from (5) by the relation $m^*(\hat{\epsilon}) = (\hbar^2/2\pi) dA(\hat{\epsilon})/d\hat{\epsilon}$. Here we have used $\hbar v_{\perp}(\hat{\xi}) = (d\hat{\epsilon})/(d\hat{\rho}) = dE/dk_{\perp}$, and $\rho(\hat{\xi})$ is the radius vector in the $\hat{\xi}$ direction. Thus the same¹¹ spherical harmonic expansion inversion scheme as was applied to convert areas to radii, may be used to invert orbital Dingle temperatures. The new relations are:

$$m^*(\hat{\epsilon}) T_{\text{orb}}(\hat{\epsilon}) \leftrightarrow \frac{\hbar}{2\pi} T_{\text{pt}} \rho(\hat{\xi})/v_{\perp}(\hat{\xi}) \quad (7a)$$

$$m^*(\hat{\epsilon}) \leftrightarrow \frac{\hbar}{2\pi} \rho(\hat{\xi})/v_{\perp}(\hat{\xi}) \quad (7b)$$

where again the spherical harmonic expansion coefficients of left and right hand sides are related by

$$a_l^m = c_l^m P_l(0) \quad (8)$$

Since $\rho(\hat{\xi})/v_l(\hat{\xi})$ scales out in calculating the ratio of the two right hand sides of (7), it need not be calculated explicitly.

b) Expansions

We now take up the relationship of accuracy and the number of useful expansion coefficients. This is particularly important since the derived point Dingle temperature, $T_{pt}(\vec{k})$, has a variable error as a function of $\vec{k}$. We do not think this has been stressed before.

For simplicity, we will assume that the error in each of the orbital Dingle temperatures T_i is uniform (~10%) although clearly high symmetry points as [100] and [111] have considerably less error than off-axis points. The corresponding orbital masses m_i , have much smaller errors, of the order 1-2%, so that these errors can be completely neglected compared to those in T_i . Thus we need consider only the error in T_i .

We wish to expand the product $m_i T_i$ and m_i as:

$$m_i T_i = \sum_j S_{ij} a_j \quad (9)$$

$$m_i = \sum_j S_{ij} b_j$$

where the S_{ij} 's are the spherical (cubic) harmonics and the a 's and b 's are the expansion coefficients. By assumption, m_i has no error, so the quality of the expansion j is governed by the a 's above. We assume that a_j has an ensemble of values, based on the range of each T_i , with a maximum likelihood¹² value a_j^* . Since

we expand $m_i T_i$, we have the product error σ_i where for the present case $\sigma_i = 0.10 m_i T_i$.

As usual we define a data vector $\vec{X}$ and a measurement matrix $\vec{M}$ by:

$$X_j = \sum_{i=1}^N S_{ij} m_i T_i / \sigma_i^2 \quad (10)$$

$$M_{jl} = \sum_{i=1}^N S_{ij} S_{il} / \sigma_i^2 \quad (11)$$

whose least squares (maximum likelihood) solution for the expansion of $m_i T_i$ is

$$a_j^* = \sum_l M_{jl}^{-1} X_l \quad (12)$$

The standard error in a_j squared is

$$(\Delta a_j)^2 = \langle (a_j - a_j^*)^2 \rangle = M_{jj}^{-1} \quad (13)$$

As we discussed above the error in the set of mass coefficients b , will have a smaller error. Let the expansion coefficient of the rhs of (7) be c and d respectively, related¹¹ to a and b by $\begin{pmatrix} a \\ b \end{pmatrix} = P_j(0) \begin{pmatrix} c \\ d \end{pmatrix}$. The standard error in c is in general bigger than that of a and is given by

$$(\Delta c_j)^2 = (\Delta a_j)^2 / P_j(0)^2. \quad (14)$$

We wish to know the derived error in T_{pt} , the point Dingle temperature. We assume that the error in

$$\pi/2\pi \rho(\hat{\xi})/v_{\perp}(\hat{\xi}) = \sum_j d_j S_{jm} \quad (15)$$

is zero. Thus the error is governed by the expansion

$$z = (\pi/2\pi)\rho(\hat{\epsilon})T_{pt}(\hat{\epsilon})/v_{\perp}(\hat{\epsilon}) = \sum_j c_j s_{jm}. \quad (16)$$

The variance or mean square deviation is

$$\begin{aligned} \langle (z - \bar{z})^2 \rangle &= \langle \left[\sum_j (c_j - \bar{c}_j) s_{jm} \right]^2 \rangle \\ \langle (z - \bar{z})^2 \rangle &= \sum_j \sum_k \frac{s_{jm}}{p_j} \frac{s_{km}}{p_k} \langle (a_j - \bar{a}_j)(a_k - \bar{a}_k) \rangle \\ &= \sum_j \sum_k \langle s_{jm}/p_j \rangle \langle s_{km}/p_k \rangle M_{jk}^{-1} \end{aligned} \quad (17)$$

So that the error in T_{pt} is given by the ratio of the square root of (17) divided by the right hand side of (7b).

Results and Discussion

A complete set of data for all angles was obtained only on the hole octahedron centered at H (and only in the Mo(W), Mo(Ru) and Mo(Fe) alloys). Effective masses (m^*) were measured to within 2% on this sheet and are shown in Fig. 1. The masses of Leaver and Meyers¹³ (used in our original publication⁵ of Mo(W) results) are also shown in the figure. The large discrepancies are obvious and resulted in erroneous derived Dingle temperatures. We believe that the discrepancies are most likely due to magnetic interaction effects which become significant in very pure samples and at high fields. We did not encounter these difficulties in our alloy samples but did see them in very pure Mo.

The Dingle temperatures obtained on the hole octahedron are shown in Fig. 2 for the (100) and (110) planes. Any anisotropy that is observed falls for the most part within experimental error. Only in Mo(Ru) do we get an anisotropy which is somewhat larger than the experimental error of 5% to 10%. But even here the small peaks near [100] occur in a region where $df/d\theta$ is large (f is the frequency and θ is the angle) thus leaving room for argument that in this region we are underestimating our errors. The Mo(Fe) and Mo(W) curves are best fit by a straight line.

Fig. 3 shows a plot of the average T_D in each material vs. $1/RRR$ (residual resistance ratio). It can be seen that all the points lie very well on one curve whose intercept is less than 0.1°K . Thus it can be argued that there was little strain in these samples and that phase smearing was relatively small; i.e., dislocation scattering which does not contribute significantly to the resistivity, appears to be less than 0.1°K .

The Mo(Ru) data was inverted, using the above described inversion technique, to obtain point Dingle Temperatures. Although the orbital temperatures are nearly flat a seemingly large anisotropy can be accidentally obtained in the point lifetimes owing to the large anisotropy in the effective masses. For this reason it is imperative that errors be analyzed carefully.

In Fig. 4 we plot the derived point Dingle temperatures for Mo(Ru) using cubic harmonic analysis. The bars in the figure mark the errors obtained using two expansion coefficients and assuming a constant 10% error in T_{orb} . As can be seen, the error in T_{pt} is quite variable being 13.3%, 34.0%, and 8.3% at [110], [111] and [100], respectively.

We list in Table I the resulting cubic harmonic coefficients and errors for a series of low order expansions. As can be seen from the table, the error in T_{orb} (10% compared to the variation of 15%) means that the variation in the $n = 2$ plot is just significant. The rather large error of 0.076 for a_3

suggests that the $n = 3$ expansion is insignificant. Since the rms fitting error for $n = 2$ fitting to $m_1 T_1$ is smaller than the assumed experimental error of 10%, the series must be cut off at $n = 1$; i.e., the data are equally well fit by a flat line, which implies a constant point Dingle temperature of 1.82 degrees.

Thus we conclude that as far as scattering on the octahedron is concerned, the resulting point lifetimes are isotropic to about 5% in all systems investigated, even though the effective mass varies from 0.75 to 1.22 electron masses and the inverse velocity varies from 0.62 to 1.92. This conclusion is consistent with the constancy of the wave functions found by Myron, Mueller and Freeman⁴ at this conference.

Using the data of Fig. 3, we find that the scattering matrix element per impurity is 0.685, 0.705, 0.711 and 0.094 eV per impurity of Ru, Fe, U and W, respectively. Thus in a simple picture the two impurities Ru and Fe have an excess of two electrons compared to Mo, U has a deficiency of two electrons, and W is homovalent. Although Fe is known to have a moment in Mo, and indeed Mo(Fe) is a Kondo system,¹⁴ it appears that all the scattering from Fe impurities can be accounted for as being due to potential scattering caused by the excess electrons. Any spin-flip scattering is smaller than our experimental error.

The data obtained on other sheets of the Fermi surface in the Mo(U) system are shown in Table II. The Dingle temperatures on the lens are smaller (just outside the range of experimental error) than the octahedron, jack and neck Dingle temperatures, the latter three of which appear to be identical. This too is consistent with the results of Myron⁴ et. al. who find that all these surfaces are almost purely d-like.

The wave functions on the ellipsoids, however, have considerable p-character and the calculated point lifetimes are a factor of two smaller than on the d-like surfaces. Our measured lifetimes appear to be either the same or even larger than on the octahedron. It is necessary to point out, however, that

although our plots of log (amplitude) vs $1/H$ had a very small rms error, nearly all the ellipsoid frequencies are degenerate in the planes measured and we could be on the tail of a long beat if we are not exactly in the plane. Since our 0.5° error in orientation is probably sufficient to cause long beats there is some doubt about the numbers obtained on the ellipsoid.

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TABLE I

#	a_1	Δa_1	a_2	Δa_2	a_3	Δa_3	Rms [*]
1	5.528	0.106	0	0	0	0	23.6
2	5.801	0.110	0.883	0.096	0	0	5.85
3	5.792	0.111	0.895	0.096	0.053	0.076	4.55

*Rms is in % and = mean error/ $\langle m_1 T_1 \rangle$

TABLE II

Dingle Temperatures for Mo(U)

Sheet	Frequency $\times 10^6$ Gauss	Orientation	T_{orb}
Octahedron	103	[111]	1.34 ± 0.05
Octahedron	151	[100]	1.28 ± 0.05
Jack	85	[111]	1.32 ± 0.05
Lens	5.2	[100]	1.12 ± 0.1
Lens	8.2	[100]	1.14 ± 0.1
Neck	13	10° from [100]	1.3 ± 0.1
Ellipsoid*	23	[100]	1.26
Ellipsoid*	28	15° from [100]	2.56

* Error not known

FIGURE CAPTIONS

- Fig. 1. Effective masses on the hole octahedron of the Fermi surface of Mo in (100) and (110) planes. The dashed curve are the data of Leaver and Meyers¹³. The masses with value ≈ 1.0 near [111] are for the electron jack.
- Fig. 2. Measured orbital Dingle temperatures on the hole octahedron in the (100) and (110) planes for three substitutional impurities in Mo.
- Fig. 3. Plot of average orbital Dingle temperature vs. inverse residual resistance ratio in the samples measured. The small intercept indicates small dislocation scattering.
- Fig. 4. Point Dingle temperatures obtained by inverting the Mo(Ru) data of Fig. 2.