DE HAAS–VAN ALPHEN EFFECT IN RHENIUM, NIOBIUM, AND TANTALUM*

A. C. Thorsen and T. G. Berlincourt
Atomics International, Division of North American Aviation, Inc., Canoga Park, California
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The electronic structures of many low-melting-point metals have been extensively investigated and characterized by de Haas–van Alphen (dHvA), galvanomagnetic, cyclotron resonance, anomalous skin-effect, and magnetoacoustic absorption techniques.[1] In contrast, despite considerable interest in the electronic character of transition metals,[2] there have been very few applications of such techniques to these elements[3,4] due primarily to the difficulties of obtaining single crystals of the requisite high purity. In this paper we report on the first observations of dHvA oscillations in the transition metals Re, Nb, and Ta. As will be evident from the data, the ranges of the observed dHvA parameters are similar to those observed for polyvalent low-melting-point metals.

The single crystals of Re and Nb used in this investigation were grown, respectively, by Nadler and Buehler using electron bombardment techniques. The Ta sample was prepared by Budnick using a strain-anneal technique.[5] Chase Brass and Copper Company material was used for the Re crystal which had a room-temperature to liquid-helium-temperature resistivity ratio of 540. The corresponding ratios for the Nb and Ta crystals were 56 and ≈ 600, respectively. (The liquid helium temperature resistivities were measured at 4.2°K in magnetic fields just sufficient to quench all superconductivity.) The Re and Nb samples were approximately 1 mm in diameter by 9 mm in length and were obtained from single-crystal rods by a combination of etching and spark cutting techniques. The Ta sample was cut from a 0.51-mm diameter wire and was composed of several small single crystals whose orientations varied slightly along the length of the sample. The approximate crystallographic orientations for all three samples are indicated in Table I. The pulsed-field apparatus used in this study has been described briefly.[6,7]

A complex electronic structure might well be anticipated in Re. If one assumes seven valence electrons per atom, the free-electron Fermi sphere completely encloses the first two Brillouin zones for the hexagonal lattice. In such a situation, there may exist in higher zones a number of electron and hole surfaces capable of generating dHvA oscillations. The results are suggestive of such a complex structure, for no fewer than four oscillating susceptibility terms were observed in Re with the field approximately parallel to the $[10\bar{1}0]$ direction. Three of these terms can

Table I. Periods, corresponding Fermi surface extremal cross-sectional areas, and effective masses for de Haas–van Alphen oscillations in Re, Nb, and Ta. (Estimated accuracy of periods is ±5%.)

Crystal	Magnetic field orientation	P (10^{-8} gauss^{-1})	A (10^{15} cm^{-2})	m^*/m_0
Re	$[10\bar{1}0]$	1.65	5.79	1.9 ±0.7
		6.3	1.52	0.5 ±0.05
		7.1	1.34	0.53 ±0.05
		124	0.077	<0.1
Nb	[110]	1.16	8.23	1.0 ±0.1
		1.67	5.72	1.0 ±0.1
Ta[a]	12° from [110] in (001) plane	2.02	4.73	...
		2.16	4.42	0.8 ±0.1

[a]Only one effective-mass entry appears after Ta because the required data were taken during a second run when only one term was observable.

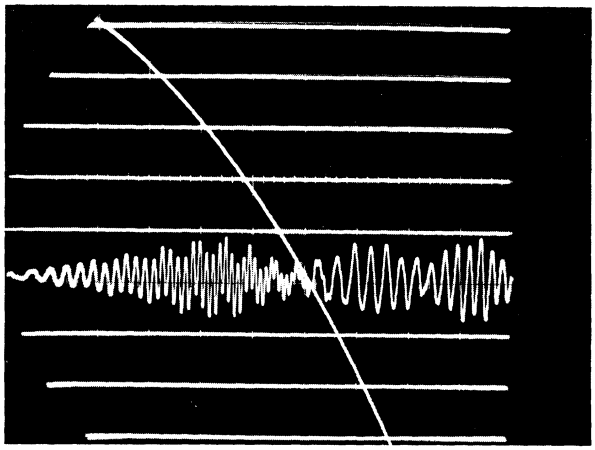

FIG. 1. de Haas–van Alphen effect in Re at 1.16°K. The oscillating trace shows the output from a pickup coil containing the sample. The curved trace shows the field increasing from 87.7 to 94.4 kilogauss during a portion of the oscillating trace. The total sweep time is two milliseconds (time increasing from right to left). Three oscillating terms are visible.

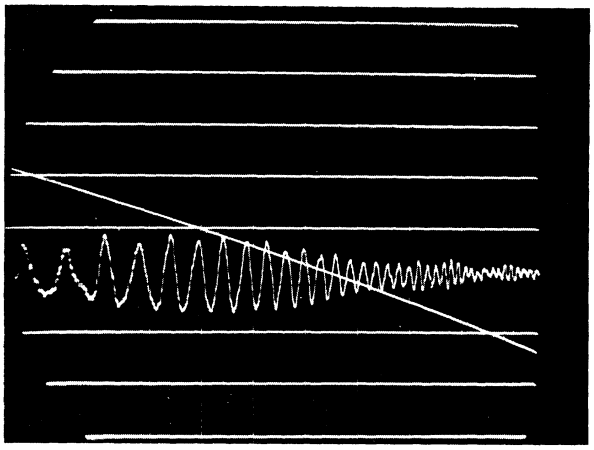

FIG. 2. Long-period de Haas–van Alphen oscillations in Re at 1.16°K. The diagonal trace shows the field increasing (from right to left) from 13.5 to 42.1 kilogauss during a sweep time of about 2.0 milliseconds.

be recognized in Fig. 1, while the fourth and much longer period term, observable at lower magnetic fields, is shown in Fig. 2. The periods P deduced from such data are given in Table I along with the corresponding Fermi surface extremal cross-sectional areas $A = 4\pi^2 e/chP$. The effective-mass values m^* listed in Table I were calculated from the temperature variations of the amplitudes of the oscillations in the usual manner.[4] It should be remarked, however, that for the longest period oscillations the corresponding m^* is so small that the exponential approximation in the temperature dependence of the amplitude was inapplicable and a comparison with the hyperbolic sine function was required. Even so, the temperature dependence of the amplitude was such that only an upper limit could be assigned to the effective mass.

The dHvA parameters in Re have values typical of those for nontransition metals. In fact, the longest period oscillations observed are comparable with those which occur in semimetals and should be easily observable with greater precision in modest magnetic fields by means of torsion balance techniques.

Two oscillating terms were observed in Nb with the magnetic field approximately parallel to a [110] direction. These are pictured in Fig. 3, and the corresponding parameters are listed in Table I. It is probable that additional oscillating terms exist but were masked by collision broadening of the Landau levels. The relatively low resistivity ratio suggests that such broadening might be quite pronounced. Little can be said as yet regarding the origin of the dHvA oscillations in Nb except that those we observe are probably not due to electrons or holes in the first two bands. The free-electron sphere completely encloses the first Brillouin zone for a pentavalent bcc metal, and on the basis of a nearly free elec-

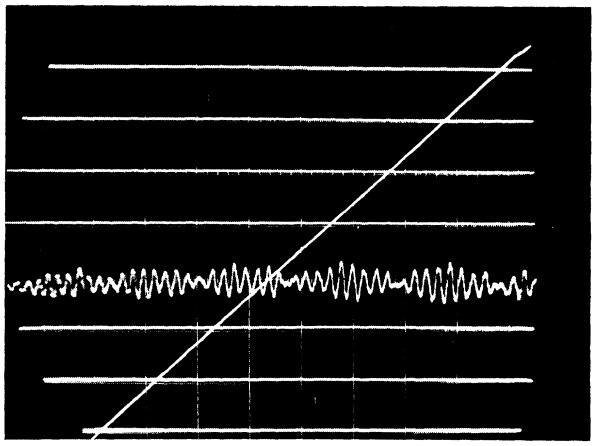

FIG. 3. de Haas–van Alphen effect in Nb at 1.14°K. The beating effect is due to two oscillating terms of different period and amplitude. The diagonal trace shows the field decreasing (from right to left) from 150.0 to 138.2 kilogauss during a sweep time of 1.6 milliseconds.

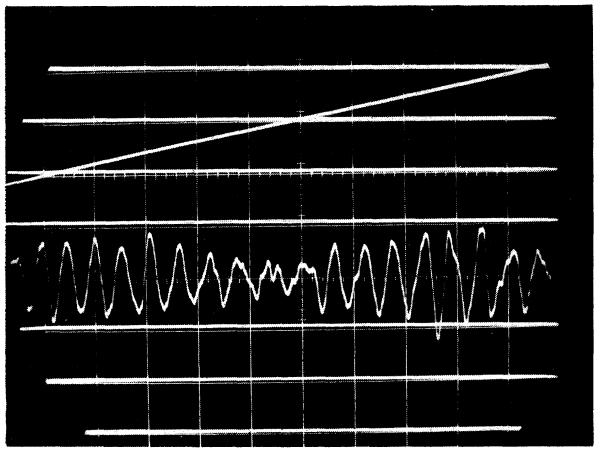

FIG. 4. de Haas–van Alphen effect in Ta at 1.13°K. The beating effect due to two oscillating terms can be seen as the field decreases (from right to left) from 141.6 to 134.9 kilogauss during a sweep time of 1.0 millisecond.

tron model[8,9] the holes in the second band would be expected to give rise to periods shorter than those observed.

Two oscillating terms were also observed in Ta (see Fig. 4), and the corresponding dHvA parameters are listed in Table I. Our measurements indicate that the shorter period term is quite sensitive to orientation, for it nearly disappeared when the sample was removed and remounted at a slightly different angle. It is interesting that Ta and Nb have the same valence and crystal structure, and have lattice parameters differing by less than one percent. For such a situation the nearly free electron model predicts almost identical periods. The observed differences (less than 50%) could be attributed to the difference in crystallographic orientation.

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[2]For a review see C. Herring, J. Appl. Phys. 31, 3S (1960).

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FERROMAGNETIC EXCHANGE INTERACTION BETWEEN Mn^{2+} IONS IN Mn, ZnF_2

M. R. Brown, B. A. Coles, and J. Owen*
Clarendon Laboratory, Oxford, England

and

R. W. H. Stevenson
Marischal College, University of Aberdeen, Aberdeen, Scotland

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Paramagnetic resonance techniques have been used to measure exchange interactions between nearest neighbor (nn) Mn^{2+} ions in mixed crystals of Mn, ZnF_2 with Mn:Zn $\approx$ 1:50. The two ions are separated by the short edge ($c \approx 3.2$ A) of the body-centered tetragonal unit cell. The general procedure has followed that used for previous investigations[1,2] of exchange-coupled pairs of spins, $S^i = S^j = \frac{5}{2}$.

The results can be described by the following spin Hamiltonians. For one ion of the pair, omitting interactions with the other ion,

$$\mathcal{H}^i = g\beta\vec{H}\cdot\vec{S}^i + D_c[(S_z^i)^2 - \tfrac{1}{3}S^i(S^i+1)] + E_c[(S_x^i)^2 - (S_y^i)^2], \quad (1)$$

where $g=2$, $S^i = \frac{5}{2}$, $D_c = -0.0135 \pm 0.004$ cm^{-1}, E_c