nonlocal-nonlinear considerations rigorously prove the $D^{-3/2}$ dependence of the critical field according to (2.46). This result [that is, $H_c/H_{cb}=\sqrt{2}h_e(0)$] is represented by the asymptotes in the upper left-hand part of Fig. 13. For $D/\lambda_0>(D/\lambda_0)_{\text{crit}}$, that is, for first order transition, the maximum fields have been determined numerically between discrete points of the equation of state. Figure 13 shows that, for fixed ξ and λ_0, the maximum field decreases with increasing thickness, but for fixed D and λ_0, the maximum field increases with ξ.

(*c*) *Comparison with Toxen's critical fields.* The maximum fields calculated by the methods of the present paper have been compared with Toxen's critical fields which were obtained from a different model.[6] In the thin-film limit, the present result (2.46) and Toxen's result for random scattering are equivalent. In Fig. 14, this result is represented by the asymptote (2a). In the general case (that is, for thicker films) the present maximum fields for diffuse scattering (curve 2) are higher than Toxen's critical fields for specular reflection (curves 1, 1a), but, qualitatively, they show the same behavior.

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Low-Field de Haas–van Alphen Studies of Chromium Group Transition Elements

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De Haas–van Alphen measurements up to fields of 18 kG have been made on the chromium group of transition elements. The results indicate that only in the case of molybdenum do the relevant parts of the Fermi surface agree well with the Lomer model. For chromium the disagreement is very marked and results presumably from its antiferromagnetic ordering at low temperatures. Possible reasons for the behavior of tungsten are discussed.

I. INTRODUCTION

THE band structure of the chromium group of transition metals is of great experimental and theoretical interest. In the case of tungsten and molybdenum, magnetoresistance[1] and anomalous skin effect measurements[2] have shown that the Fermi surface of each metal is essentially compensated in character. The effective area of the Fermi surface is, moreover, less than that corresponding to a sphere containing one electron per atom, so that the free electron model is certainly not applicable to these metals.

Lomer[3] has recently advanced a model which is consistent with these results. Essentially, the proposed model postulates the existence of star-shaped electron and hole surfaces, situated at the zone center and zone corners, respectively. These surfaces, which contain roughly equal numbers of carriers, are degenerate along ⟨100⟩. Additional hole pockets are present at the centers of the zone faces, while along the cube axes are further small groups of electrons or holes. A similar band structure is predicted for nonmagnetic chromium. Lomer has considered the effects of antiferromagnetic ordering in the latter, but it is not clear what detailed modifications this would cause in the associated Fermi surface.

Recent dHvA[4] and magnetoacoustic[5] measurements have shown that, in the case of tungsten, the major parts of the Fermi surface are in essential agreement with the above model. This conclusion does not, however, apply to the small pockets of carriers along ⟨100⟩, neither set of data giving very complete information in this regard. Since the existence of these pockets is an essential feature of the model, detailed measurements of the low-field dHvA effect in tungsten are needed to investigate their presence and nature. In addition, a comparison with the dHvA effect in molybdenum and chromium is necessary to establish the consequences of antiferromagnetic ordering in the latter. For these reasons the present study[6] was undertaken.

The results indicate that only in molybdenum does the Lomer model provide an adequate description of the relevant part of the Fermi surface. In the case of tungsten additional periods are observed, one set of which are attributable to extremal orbits around the necks of the main electron surface. The remaining periods are

[1] E. Fawcett, Phys. Rev. **128**, 154 (1962).
[2] E. Fawcett and D. Griffiths, J. Phys. Chem. Solids **23**, 1631 (1962).
[3] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).
[4] R. F. Girvan and A. V. Gold (private communication).
[5] J. A. Rayne and H. Sell, Phys. Rev. Letters **8**, 199 (1962).
[6] Preliminary results have already been reported: G. B. Brandt and J. A. Rayne, Phys. Letters **3**, 148 (1962); see also D. Sparlin and J. A. Marcus, Bull. Am. Phys. Soc. **8**, 258 (1963).

tentatively attributed to the effects of spin-orbit splitting on the band structure. For chromium, the disagreement with the Lomer model is probably due to the antiferromagnetic ordering occuring at low temperatures.

II. EXPERIMENTAL TECHNIQUE

Measurements of the dHvA effect were made up to 18 kG, using an automatic recording torsion balance described previously.[7] The specimens of tungsten and molybdenum were single crystals of electron-beam melted material, produced by Westinghouse Lamp Division, Bloomfield, New Jersey. These had, respectively, residual resistance ratios of 25 000 and 3000 to 1. In both cases three cylindrical specimens were used, the cylinder axes being [100], [110], and [111]. For the experiments on chromium, a single crystal, produced by Dr. B. Gonser of Battelle Memorial Institute, was employed. This crystal, which was produced by a vapor deposition process, had a resistance ratio of approximately 1500 to 1. Well developed {111} facets were present on the crystal, thereby easily enabling the sample to be oriented with the three principal directions vertical. All data were taken at approximately 1.3°K. No difficulties due to eddy currents were encountered owing to the high magnetoresistance of each metal.

III. RESULTS

The results of the measurements are given in Figs. 1 through 8. It is noted that the frequency $f(1/H)$, rather than period $\Delta(1/H)$, has been plotted in these graphs. This method of presentation has the advantage that the former quantity is directly proportional to the associated extremal area. Thus we have

$$f(1/H)=[\Delta(1/H)]^{-1}=\hbar cA/2\pi e. \quad (1)$$

In the case of chromium, a number of frequencies have been observed in addition to those shown in Figs. 7 and 8. These are listed in Table I, which summarizes the relevant data for all three metals. It is believed that the over-all accuracy of the entries is of the order of two percent.

IV. DISCUSSION

Figure 9 shows an extended cross section, in a (100) plane, of the proposed Fermi surface for the chromium group of transition metals. As noted previously, the main groups of carriers are contained in the star shaped

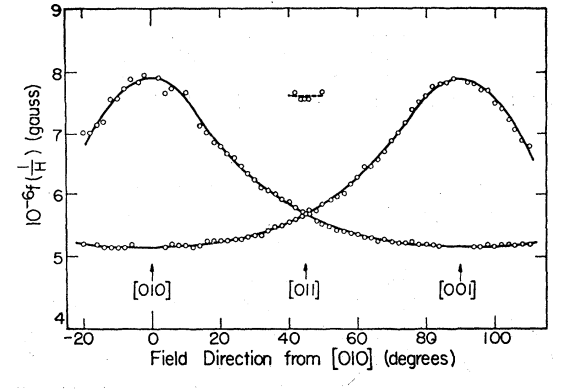

FIG. 1. Variation with field direction of dHvA frequencies in Mo for [100] axis of suspension.

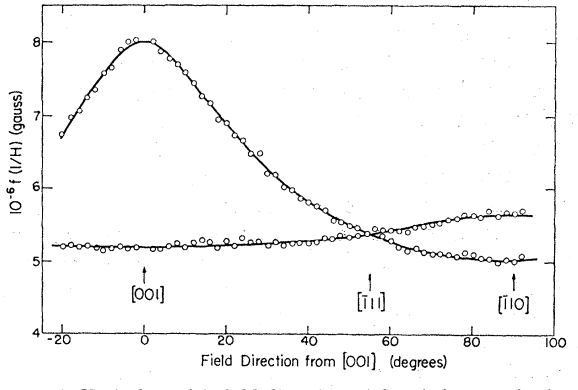

FIG. 2. Variation with field direction of dHvA frequencies in Mo for [110] axis of suspension.

[7] G. B. Brandt and J. A. Rayne, Phys. Rev. **132**, 1512 (1963).

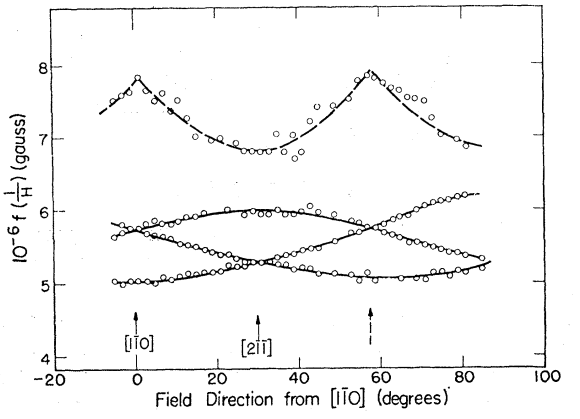

FIG. 3. Variation with field direction of dHvA frequencies in Mo for [111] axis of suspension. The lack of symmetry in the rotation pattern is due to a slight specimen misalignment.

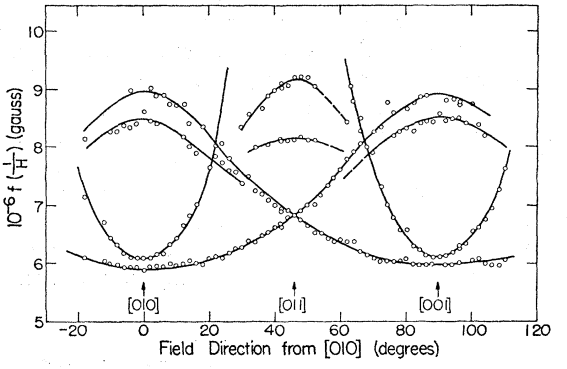

FIG. 4. Variation with field direction of dHvA frequencies in W for [100] axis of suspension.

electron and hole surface at Γ and H, respectively. The carriers which are presumably relevant to the present work, however, are the electrons or holes along $\langle 100 \rangle$, and possibly the holes at N. The presence of the former results from the crossing of the bands Δ_2 and Δ_2' in the vicinity of the cube axes. Depending on whether the Fermi level is above or below the crossover point, the pockets contain either electrons or holes. As has been pointed out by Lomer, it is impossible to avoid their presence without a complete reassessment of the band structure. Thus, the existence and nature of these surfaces is of crucial importance in assessing the accuracy of the model.

Reference to Figs. 1 through 3 shows that the behavior of molybdenum is in reasonable accord with the Lomer model, assuming that the pockets are approximately oblate spheroids with minor axes along $\langle 100 \rangle$. Thus in Fig. 2, which corresponds to a rotation of H in a (110) plane, only two branches are observed. The shallow branch is associated with the equivalent pockets along [010] and [100], while the steep branch is associated with the pockets along [001]. It may readily be verified that an assumption of prolate spheroids is inconsistent with the observed magnitudes of $f(1/H)$ along [001] and [110]. Actually the spheroids are not in fact surfaces of revolution, but are slightly elongated along the cube directions lying perpendicular to their minor axes. This would then explain the difference between the lower values of $f(1/H)$ for $H \| [001]$ and $H \| [110]$.

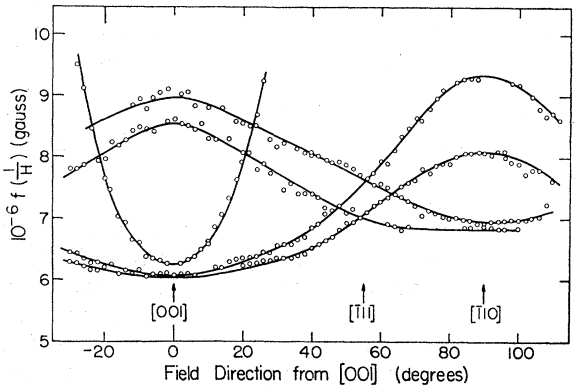

FIG. 5. Variation with field direction of dHvA frequencies in W for [110] axis of suspension.

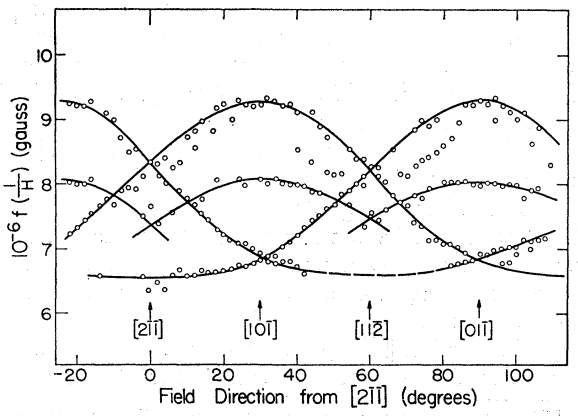

FIG. 6. Variation with field direction of dHvA frequencies in W for [111] axis of suspension.

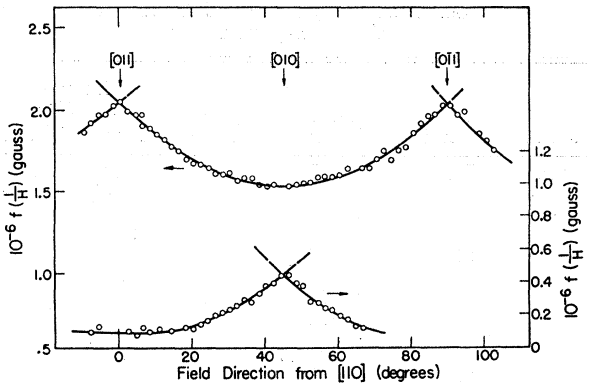

FIG. 7. Variation with field direction of dHvA frequencies in Cr for [100] axis of suspension.

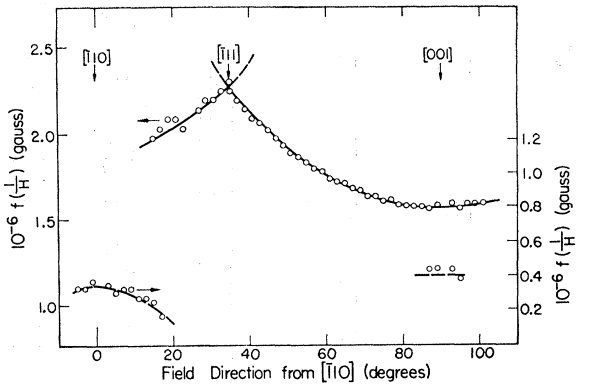

FIG. 8. Variation with field direction of dHvA frequencies in Cr for [110] axis of suspension.

If the dotted sections are for the moment disregarded, the rotation diagrams of Figs 1 and 3 are also consistent with the above hypothesis. In the former only two branches, corresponding to the pockets along [010] and [001], are observed. The couple due to that along [100] is very small and probably is undetectable, since the associated extremal area is essentially independent of field orientation. From Table I, it may be seen that there is reasonable agreement between the observed and theoretical extremal areas. Thus, the Lomer model seems to be in good accord with the experimental data, except for the above-mentioned unassigned frequencies. These certainly do not appear to find a ready explanation within the framework of the model. It seems scarcely possible to associate them with the hole surfaces at N, since the associated extremal areas are too small. Similarly, there is no obvious way in which the

TABLE I. Summary of low-field dHvA data for chromium-group metals.

Metal	Axis of suspension	Field direction	$f(1/H)$ (10^6 G)	Extremal area (Å^{-2}) Expt'l.	Theory
Mo	[100]	[010]	7.92	0.076	0.04
			5.15	0.049	0.04
		[011]	7.68	0.073	···
			5.70	0.054	0.04
	[110]	[001]	8.00	0.076	0.04
			5.17	0.049	0.04
		[$\bar{1}$11]	5.37	0.051	0.04
		[$\bar{1}$10]	(24.2)[a]	(0.23)	(0.16)
			5.63	0.054	0.04
			5.03	0.048	0.04
	[111]	[1$\bar{1}$0]	(25.8)	(0.25)	(0.16)
			7.67	0.073	···
			5.75	0.055	0.04
			5.04	0.048	0.04
		[2$\bar{1}\bar{1}$]	6.79	0.065	···
			5.97	0.057	0.04
			5.28	0.050	0.04
W	[100]	[010]	8.90	0.085	0.04
			8.46	0.081	0.04
			6.08	0.058	0.06
			5.94	0.057	0.04
		[011]	9.22	0.088	0.04
			8.12	0.078	0.04
			6.78	0.065	0.04
	[110]	[001]	8.98	0.086	0.04
			8.55	0.082	0.04
			6.24	0.060	0.06
			6.03	0.058	0.04
		[$\bar{1}$11]	7.62	0.073	0.04
			7.01	0.067	0.04
		[$\bar{1}$10]	9.28	0.089	0.04
			8.07	0.077	0.04
			6.90	0.066	0.04
	[111]	[1$\bar{1}$0]	9.27	0.089	0.04
			8.05	0.077	0.04
			6.85	0.065	0.04
		[2$\bar{1}\bar{1}$]	8.22	0.079	0.04
			7.57[b]	0.072	0.04
			6.52	0.062	0.04
Cr	[100]	[010]	9.87[c]	0.094	···
			5.80[c]	0.055	0.04
			1.53	0.014	···
			0.45	0.004	···
		[011]	11.0[c]	0.105	···
			8.78[c]	0.084	···
			4.83	0.046	0.04
			2.05	0.019	···
			0.10	0.001	···
	[110]	[001]	8.12	0.077	0.04
			6.03	0.060	0.04
			1.57	0.015	···
			0.42	0.004	···
		[$\bar{1}$11]	10.4	0.100	···
			4.93	0.047	0.04
			2.30	0.022	···
		[$\bar{1}$10]	4.93	0.047	0.04
			0.41	0.004	···

[a] Values in parenthesis are presumably due to holes at N.
[b] Mean value of unresolved beat pattern.
[c] Approximate value only.

E versus k curves can be modified to give additional small pockets of carriers, except possibly to invoke the effects of spin-orbit splitting. A discussion of this hypothesis is deferred until the results for tungsten are presented.

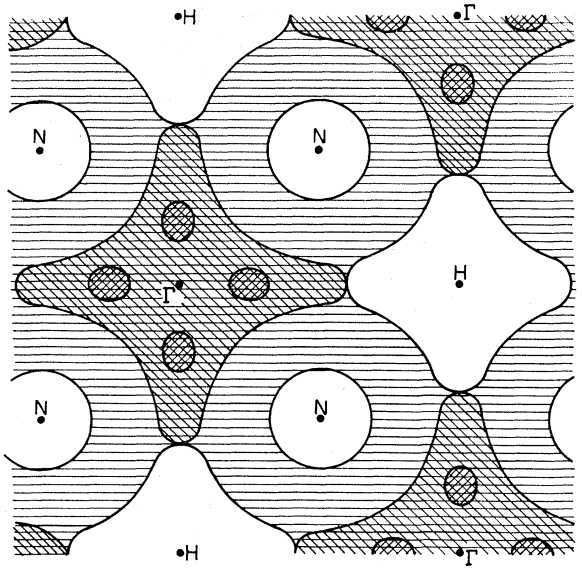

FIG. 9. Extended cross section in (100) plane for Fermi surface of chromium group transition metals, according to Lomer (Ref. 3).

Reference to Table I shows that for the [110] and [111] suspensions, with $H\sim[\bar{1}10]$, a much higher frequency oscillation is observed. This oscillation is detectable over about a twenty degree interval on either side of [$\bar{1}$10] for a [110] suspension and is undoubtedly due to the hole surface at N. There is reasonable agreement between the observed and theoretical extremal areas.

Figures 4 through 6 show the rotation diagrams obtained for tungsten. It is at once apparent that they are far more complex than those for molybdenum. The most obvious difference concerns the rapidly changing frequency observed for $H\sim\langle 100\rangle$. This oscillation, which is visible only over a narrow angular interval away from the symmetry direction, is probably due to an orbit around the necks of the electron surface at Γ.[8] As may be seen from Fig. 9, these necks are quite elongated in the direction of the cube axes, and it does not seem unreasonable to suppose that they do, in fact, possess an extremal cross section. The rapid change of frequency as a function of field direction suggests that the necks are of roughly hyperboloidal rather than cylindrical shape. Because of the limited range over which an extremum is possible, the oscillations are not observed for a [111] suspension.

A comparison of Figs. 2 and 5 shows that, in tungsten, there appear to be two sets of pockets along the cubic axes and that they are approximately prolate, rather than oblate, spheroids with their major axes along $\langle 100\rangle$. From the difference in values of $f(1/H)$ for $H\|[001]$ and $H\|[\bar{1}10]$, it further appears that the spheroids are not exact surfaces of revolution but that

[8] This assignment was first proposed by D. Sparlin, Ref. 6. It finds support in the results of recent magnetoacoustic data on tungsten. See J. A. Rayne, Phys. Rev. **131**, 653 (1963).

they are somewhat distorted. Since it is not clear which branches are related to each other, the exact value of this distortion cannot be specified further. The behavior for the [100] and [111] suspensions, shown in Figs. 4 and 6, is also consistent with the above picture. In the former, for $H\sim[110]$, the upper curves are certainly due to the pockets aligned along [100]. The magnitude of the couple due to these pockets is larger than in the case of molybdenum, since they deviate much more from being surfaces of revolution.

There remains the problem of explaining the multiplicity of carriers observed in tungsten. The only reasonable possibility is that the Lomer model neglects the effects of spin-orbit splitting on the band structure. These effects would, of course, be most important in the metal highest atomic number, viz., tungsten, and could easily cause the observed doubling, since the spin degeneracy of all levels, and in particular Δ_2 and Δ_2', would be lifted. The doubling would undoubtedly be present in all the surfaces, but presumably would be most apparent in the pockets of carriers along ⟨100⟩, since they are the smallest. As has been mentioned previously, this spin splitting could also account for the extra oscillations observed in molybdenum. No evidence for the effect has been seen either in magnetoacoustic or high-field dHvA data in either metal. Extremely careful measurements would, however, be required to detect any significant doubling of the larger pieces of Fermi surface. Further experiments to elucidate this point are clearly desirable.

The situation with regard to chromium is quite different from the other two metals. In addition to the oscillations having roughly the frequency 5×10^6 G, additional oscillations having about double this frequency, as well as those shown in Figs. 7 and 8, are observed. Moreover, preliminary magnetoresistance studies[9] have shown that open orbits are present in chromium, so that the Fermi surface of Fig. 9 cannot be correct. It would seem that the most likely reason for the breakdown of the Lomer model is that chromium is antiferromagnetic below room temperature. *A priori* it is difficult to predict what modifications to the surface are caused by this magnetic ordering. Overhauser[10] has treated the effects of antiferromagnetism on the band structure of an electron gas with a spherical Fermi surface, using the method of spin density waves. The resulting magnetic energy gaps introduce necks in the sphere, along the direction of the propagation vector of the spin density wave. These necks result from the incommensurability of the wave-number vector associated with the magnetic order, and of the reciprocal lattice. Extending these ideas to the case of chromium, Overhauser predicts the existence of six such truncated faces for both the electron and hole surfaces of Fig. 9. The estimated radius of these truncated sections is $R_0\sim0.2\times10^8$ cm^{-1}, which corresponds to an area of 0.12 Å^{-2}. This estimate seems to be in accord with the extremal area corresponding to higher frequencies shown in Table I and it does not seem unreasonable to associate the two.

The present data are not sufficiently accurate to enable the rotation diagrams of the intermediate and high frequencies to be followed with any accuracy. It is thus difficult to determine unequivocally, whether or not the former are associated with pockets of carriers along ⟨100⟩. In addition, there remains the difficulty of explaining the existence of the branches shown in Figs. 7 and 8, together with an even lower frequency oscillation reported by Montalvo *et al.*[11] Even more serious is the difficulty of explaining, even within this modified Lomer model, the existence of open orbits in chromium. Much more extensive data, at higher fields on much better samples, are needed to resolve these questions.

Owing to the extreme complexity of the beat patterns encountered in this study, little effort has been made to study the effective masses of the carriers in any of the metals. For molybdenum, in a [100] suspension with $H\sim[011]$, the effective mass ratio for the dominant period is $m=0.29$. No corresponding value has been reported from cyclotron resonance data,[12] the lowest quoted figure being a group of carriers with $m\sim0.5$. It would thus appear that the latter experiments have only detected the masses associated with larger pieces of the Fermi surface.

In summary, it seems that the Lomer model gives an adequate description of the Fermi surface of molybdenum and tungsten, apart from possible effects due to spin-orbit splitting. For the case of chromium there are complications arising from the effects of antiferromagnetism and much more work is needed to establish the nature of its Fermi surface.

ACKNOWLEDGMENTS

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[10] A. W. Overhauser, Phys. Rev. 128, 1437 (1962).
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