The technical importance of $3d^4$ systems and possibly $3d^6$ systems for masers operating at frequencies of several hundred kMc/sec, coupled with the observation of rather narrow lines and fairly long relaxation times, makes the study of Mn^{3+}, Cr^{2+}, and Fe^{2+} ions of interest.

ACKNOWLEDGMENTS

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Low-Field de Haas–van Alphen Effect in Indium

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De Haas–van Alphen data for indium, up to fields of 18 kG, have been obtained using an automatic torsion balance. The resulting extremal areas agree qualitatively with the third zone surface predicted by the free-electron model. A detailed comparison shows, however, that the experimental areas are considerably smaller than those given by the single orthogonalized plane-wave theory and that the arms are close to being cylindrical over a considerable part of their length. For certain ranges of field orientation, the amplitude of the oscillatory susceptibility is much lower than would be expected. An explanation of this effect is considered.

I. INTRODUCTION

THE free-electron model[1] gives surprisingly accurate predictions concerning the Fermi surface of indium, at least insofar as the second-zone surface is concerned. Less information concerning the third-zone surface is available and it is of interest to know whether this also conforms to a single orthogonalized plane wave (OPW) model. Low-field de Haas–van Alphen (dHvA) data would be very helpful in settling this question. Unfortunately, however, there is considerable disagreement among the existing data.[2–4] Since the data are incomplete and are thought to be subject to errors in crystal orientation, the present series of measurements was undertaken to rectify these deficiencies. Very complete data up to 18 kG have been obtained for [100], [001], [110], [011], and [111] crystal suspensions using an automatic torsion balance. The measurements show that the free-electron model gives a correct *qualitative* description of the third-zone surface, although the extremal areas differ considerably from those obtained experimentally. In addition, the arms of the third-zone surface are almost cylindrical along a considerable part of their length. As noted by previous observers,[2] the amplitude of the oscillatory susceptibility is very small for $H \sim [001]$. A possible explanation of this effect is considered.

[1] Walter A. Harrison, Phys. Rev. **118**, 1190 (1960).
[2] D. Shoenberg, Phil. Trans. Roy. Soc. (London) **A245**, 1 (1952).
[3] B. I. Verkin, B. J. Lazarev, and N. S. Rudenko, Zh. Eksperim. i Teor. Fiz. **20**, 93 (1950).
[4] B. I. Verkin, B. J. Lazarez, and N. S. Rudenko, Zh. Eksperim. i Teor. Fiz. **20**, 995 (1950).

II. EXPERIMENTAL METHOD

Measurements of the de Haas–van Alphen effect were made using an automatic torsion balance similar to that described by Croft, *et al.*[5] Fields up to 18 kG were produced in a Harvey-Wells type-L128 electromagnet and type HS-1050 regulated power supply. A Rawson type-820 rotating coil gaussmeter, calibrated *in situ* by means of the Li^7 resonance line, was used to measure the field at the sample. Data were recorded automatically by scanning the field over an appropriate interval and

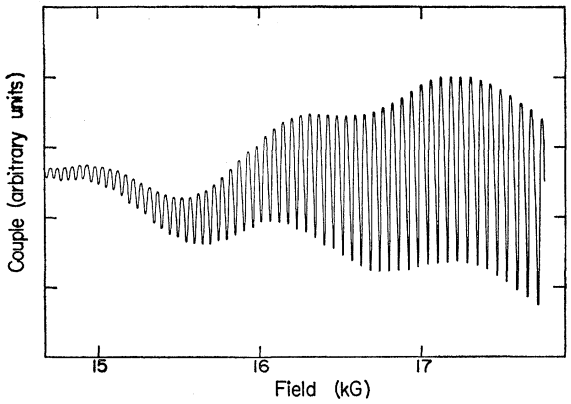

FIG. 1. Typical recorder trace of feedback current versus magnetic field with [001] axis of suspension. The field is inclined at 24° to [100]; the temperature is approximately 1.2°K.

[5] G. T. Croft, J. F. Donahoe, and W. F. Love, Rev. Sci. Instr. **26**, 360 (1955).

plotting feedback current as a function of gaussmeter reading on a Moseley type 2D2 recorder. A typical recorder tracing is shown in Fig. 1.

Indium single crystals were grown by the Bridgman technique. These were then oriented by x-rays and suitable samples cut from the ingot by means of a Servomet spark cutter. Initially, crystals of zone-refined starting material were used, but the resulting specimens gave a considerable amount of trouble because of the excessive eddy currents induced in them at normal field sweep rates. It was found more satisfactory to use standard grade indium of 99.98% purity. No difficulties were experienced in producing single crystals of this material and there was little apparent reduction in the amplitude of the oscillatory susceptibility due to impurity scattering.

De Haas–van Alphen data were obtained for crystals with [100], [001], [110], [011], and [111] axes of suspension. In all cases the measurements were made

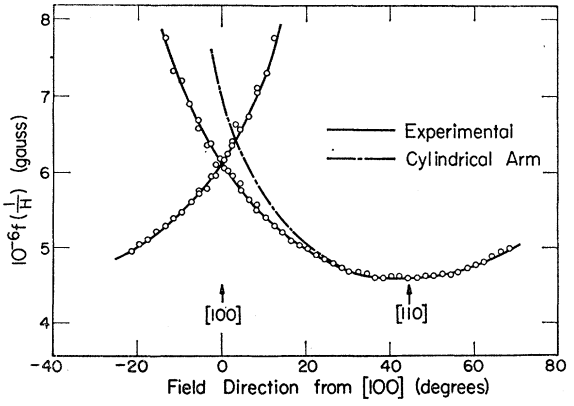

FIG. 2. Angular dependence of $f(1/H)$ on field orientation for principal oscillation with [001] axis of suspension.

at the lowest attainable temperature, approximately 1.2°K. For the [001] suspension, the temperature variation of the amplitude of the oscillatory susceptibility was also measured to obtain the effective mass of the carriers.

III. RESULTS

Both high- and low-frequency oscillations in the susceptibility were observed for most orientations; this is clearly seen in Fig. 1. The variation with crystal orientation and field direction of the high-frequency component is shown in Figs. 2 through 6. It should be noted that the *frequency* $f(1/H)$, rather than the *period* $\Delta(1/H)$, has been plotted in these graphs. This method of presentation has the advantage that $f(1/H)$ is directly proportional to the extremal area of that part of the Fermi surface being measured. It should be noted that

$$f(1/H)=[\Delta(1/H)]^{-1}. \quad (1)$$

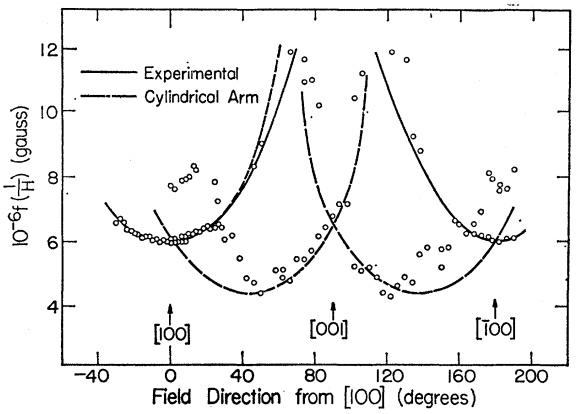

FIG. 3. Angular dependence of $f(1/H)$ on field orientation for principal oscillation with [010] axis of suspension.

Figure 7 shows the angular variation of the low-frequency component of oscillatory susceptibility for the [100] and [001] suspensions. The temperature dependence of the amplitude of the dHvA effect, for a [001] suspension with $H\|[110]$, is given in Fig. 8 as a semi-

TABLE I. Comparison of dHvA data for different axes of suspension.

Axis of suspension	Field direction	$10^{-6}f(1/H)$ (G)
[001]	[110]	4.60
	[100]	6.12
[100]	[010]	6.08
	(011)	4.38
[110]	[1$\bar{1}$0]	4.62
	[001]	5.30
[011]	[100]	6.08
	(01$\bar{1}$)	8.44
[111]	[1$\bar{1}$0]	4.57

logarithmic plot of (C/T) versus T. The principal frequency $f(1/H)$ for each axis of suspension, with the field along certain symmetry directions, is given in Table I.

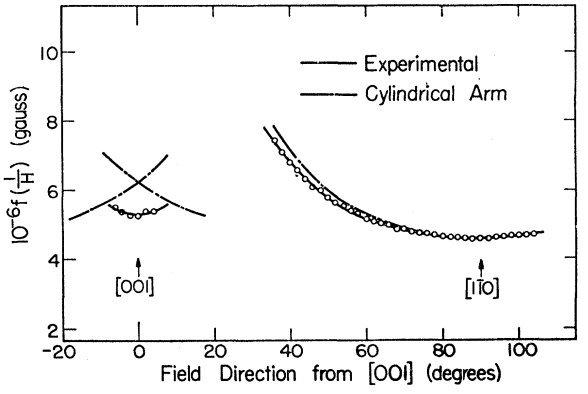

FIG. 4. Angular dependence of $f(1/H)$ on field orientation for principal oscillation with [110] axis of suspension.

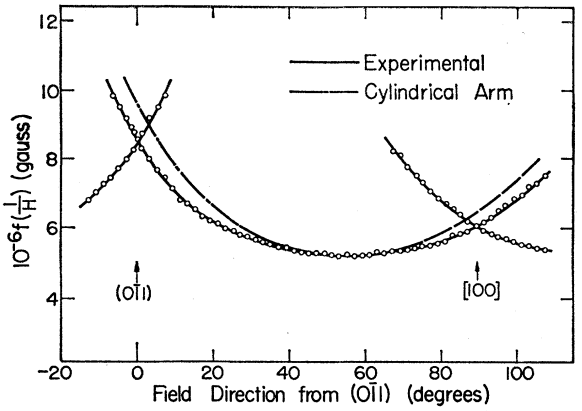

FIG. 5. Angular dependence of $f(1/H)$ on field orientation for principal oscillation with [011] axis of suspension.

IV. DISCUSSION

Reference to Figs. 2 through 6 shows that the scatter of the data, except for the [100] suspension, is considerably below one percent. It is felt that the principal systematic errors in the data arise from errors in crystal orientation (usually of the order of one degree or less), and from the difficulty of ensuring accurate crystal alignment with respect to the field. A conservative estimate of the over-all absolute accuracy is two percent. For the [100] suspension, considerable difficulty was experienced in obtaining satisfactory data, because of the rather large anisotropy of the static component of susceptibility. The resulting large couple on the torsion balance made observation of the oscillatory component very difficult with the field near [001]. Observational difficulties were compounded by the unusually small dHvA effect in this orientation and so the scatter of the data is correspondingly large. Similar difficulties were experienced using other suspensions, with the field near [001]; viz., [110] and [111]. In this connection, it should be noted that Shoenberg[2] noticed that the dHvA oscillations became vanishingly small under the same conditions. A possible reason for this effect will be considered later. It is clear, however, that the data of Verkin *et al.*[3,4] are subject to errors in crystal orientation, since their experiments indicated a vanishingly small dHvA effect with the field *perpendicular* to [001]. The present work shows that this is clearly incorrect.

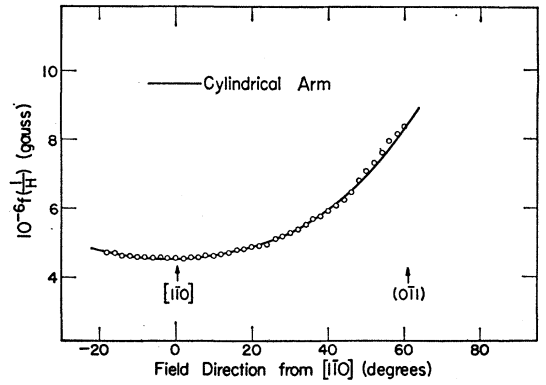

FIG. 6. Angular dependence of $f(1/H)$ on field orientation for principal oscillation with [111] axis of suspension.

For a [110] suspension, identical with that employed by Shoenberg, marked oscillatory behavior is obtained out to angle making approximately 60° with [1$\bar{1}$0]. This angular range is larger than that observed by him, and is presumably due to the greater sensitivity of the present equipment. From the dotted curve of Fig. 4, it is clear that the frequency of oscillation varies approximately as sec θ, where θ is the angle between H and [1$\bar{1}$0], again in agreement with Shoenberg.[6]

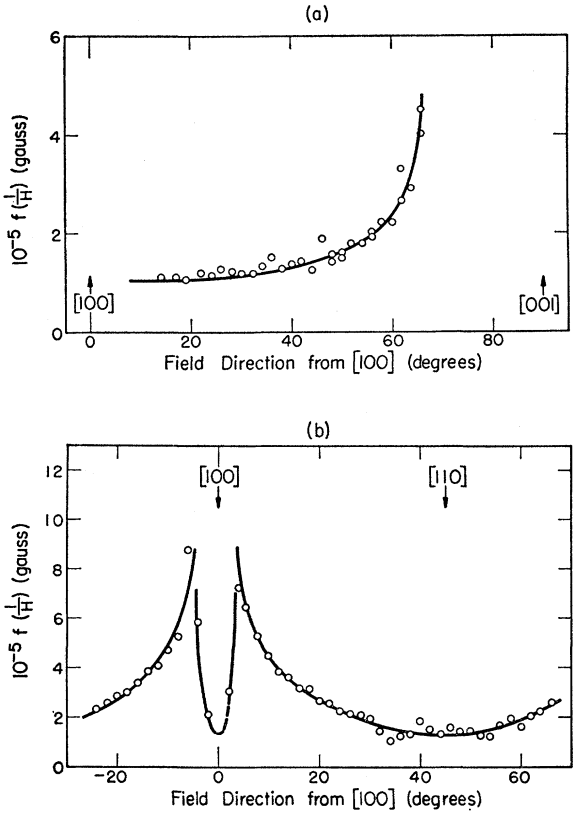

FIG. 7. Angular dependence of $f(1/H)$ on field orientation for low-frequency oscillation with [010] and [001] axes of supension.

It is believed that all the observed oscillatory behavior is due to extremal areas associated with the third-zone Fermi surface of indium. According to the free-electron model,[7] the third-zone surface is as shown in Fig. 9. Due to the tetragonal structure of indium, the arms α, β are no longer equivalent, the normal cross-sectional areas being given in Table II. For the [001] suspension, the principal oscillations are due to the arms β lying in

[6] It should be noted that the data of Shoenberg give a period $\Delta(1/H)$ varying as $\sin\psi$, where $\psi=(\pi/2)-\theta$.

[7] J. Rayne, Phys. Rev. **129**, 652 (1963).

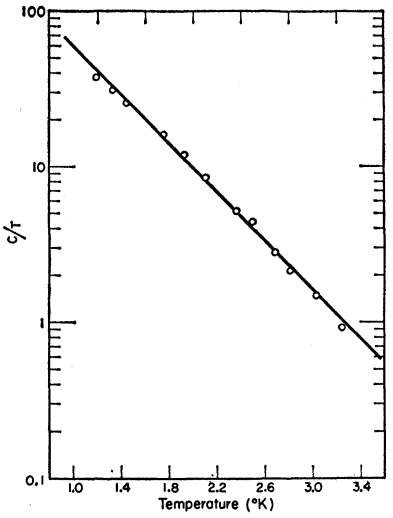

FIG. 8. Semilog of (C/T) versus temperature for [001] axis of suspension with H along [110].

the basal plane. As for other axes of suspension, the *period* of oscillation follows approximately a cosine law, showing that the arms are slightly tapered cylinders along a considerable part of their length. The beat pattern between the two pairs of arms can be followed over about ten degrees either side of the [100] direction.

For the [011] and [111] suspensions, the observed oscillatory behavior is also undoubtedly due to the arms β. As may be seen from Table I, there is good agreement between the various data. None of these suspensions, however, give any information about the α arms, which are very difficult to see. The only extensive oscillations, which can be definitely attributed to these areas, occur with the [100] suspension. Unfortunately these oscillations are quite weak and, because of previously mentioned experimental difficulties, the resulting scatter of the data is quite large. It is thus not clear whether the apparently large deviation from cylindrical symmetry is significant or not. The weak oscillations, for a [110] suspension with $H\sim$[001], are probably also due to the α arms. No beat pattern was resolvable for this orientation and it seems likely that the measured frequency is that of the *mean* arising from the two pairs of α arms.

From the observed frequencies of oscillation, the extremal areas of the α, β arms can be found from the usual formula.[8]

$$A=\frac{2\pi e}{\hbar c\Delta(1/H)}=\frac{2\pi e}{\hbar c}f\left(\frac{1}{H}\right). \qquad (2)$$

Table II gives a comparison between the normal cross sections so computed and those found from the free-electron model. As can be seen, the agreement for the β arms is quite poor, the calculated value being some 50% too *high*. Similar disagreement with the single

[8] See, for example, D. Shoenberg, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 235.

TABLE II. Comparison of single OPW and experimental areas of arms α, β.

Arm	Single OPW area (A^{-2})	Experimental
α	0.029	0.042
β	0.084	0.044 (0.044)[a]

[a] Estimated from magnetoacoustic data.

OPW model is found in aluminium[9]; it is not unexpected, since the extremal areas of small parts of the Fermi surface are quite sensitive to the nonvanishing matrix elements of the crystal potential in the many OPW approximation. It is of interest, however, that the area of the α arms appears to be *larger* than that predicted by the single OPW model.

From previously published magnetoacoustic data,[7] it is possible to estimate the area of the arms β. These are roughly triangular in shape, as shown in Fig. 9, and from the known dimensions f, g one can easily calculate the approximate extremal area. As may be seen from Table I, the agreement is very good, lending confidence to the previous assignment of the long period magnetoacoustic oscillations. Unfortunately, there is insufficient magnetoacoustic data to obtain similar estimates of the arms α.

The small amplitude of oscillations arising from the arms α has been noted by previous observers and is somewhat difficult to understand. Reference to Table I shows that the two sets of arms α, β are of roughly the same area and it seems unlikely that their shape would be appreciably different. Thus, one would expect roughly equivalent amplitudes of the oscillations. A possible explanation of the effect is that the expression for the couple on the specimen involves the so-called spin-splitting factor[8] $\cos(\pi m/m_0)$. Clearly, if $(m/m_0)\sim\frac{1}{2}$, this factor would be very small. It is conceivable that the arms α do, in fact, possess such a large effective mass, although there are no cyclotron resonance data to support this hypothesis. It is noteworthy, however, that the free-electron model predicts a much smaller mass, $m\sim 0.1\,m_0$. This model usually underestimates the actual cyclotron mass, but it seems unlikely that the

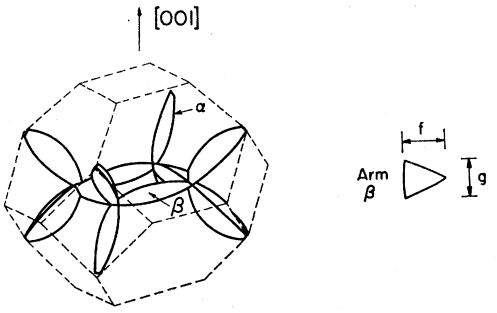

FIG. 9. Third-zone Fermi surface for indium according to free-election model.

[9] Walter A. Harrison, Phys. Rev. 116, 555 (1959).

discrepancy would be quite as large as that required here. Thus, at the moment, no resolution of the question can be advanced.

From the temperature dependence of the dHvA oscillations, the effective mass of the associated carriers can be determined readily. Thus, at a fixed field H, the couple acting on the sample can be written

$$C=\alpha T e^{-(2\pi^2 kT/\beta H)}, \tag{3}$$

where α is a constant, $\beta=(e\hbar/m^*c)$ and it is assumed that $(2\pi^2 kT/\beta H)\gg 1$. From (3) it follows that a semilog of C/T versus T is a straight line of slope $-2\pi^2 k/\beta H$, thus giving m^*. Such a plot, for an [001] suspension with $H\|[110]$, is given in Fig. 8. The resulting effective mass of the associated β arm is $(m^*/m_0)=0.19$, which is to be compared with the single OPW value of 0.11. As noted previously, such a discrepancy has been noted in many metals, most notably aluminum.[1,10] No satisfactory explanation of this disagreement has yet been advanced. Attempts to obtain effective mass data with $H\|[100]$ were not successful, due to the difficulty of obtaining an oscillatory behavior free from beats.

[10] T. W. Moore and F. W. Spong, Phys. Rev. **125**, 846 (1962).

The low-frequency oscillations observed in the present data are similar to those found by Gunnerson[11] in aluminum. It is probable that they arise from extremal areas around the ends of the arms α, β. An exact calculation of these areas is of course very difficult, since they are very sensitive to the effective lattice potential. It seems clear, however, that for $H\|[100]$, quite complicated orbits would be involved, since they correspond to junctions of four arms. This probably accounts for the rather unusual cusps in the angular variation of $f(1/H)$ shown in Fig. 7(b).

V. CONCLUSION

Low-field de Haas–van Alphen data for indium have been obtained up to fields of 18 kG. The resulting extremal areas are in qualitative agreement with the third-zone surface of the single OPW model. For certain field orientations the amplitude is much less than would be expected; a possible explanation of this effect is considered.

[11] E. M. Gunnerson, Phil. Trans. Roy. Soc. (London) **A249**, 299 (1957).

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Impurity Conduction in p-Type Silicon at Microwave Frequencies*

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The microwave conductivity of boron-doped silicon was studied at low temperature at ~9000 Mc/sec. Samples measured had boron concentrations ranging from 6.7×10^{15} to 1.6×10^{17} cm^{-3}. In the impurity conduction range, the microwave conductivity varied much more slowly than the dc conductivity, becoming orders of magnitude larger in comparison at 4.2°K. Calculations based on the hopping model give microwave conductivity of the right order of magnitude as measured. However, pronounced nonohmic behavior was observed in samples of impurity concentrations less than $\sim10^{16}$ cm^{-3}, and the measured temperature dependence of conductivity for the samples of high-impurity concentrations was too strong. These observations cannot be accounted for by the hopping model. It is shown that the nonohmic behavior may be attributed to the direct absorption of microwave power for which phonon interaction is not the essential part of the process. The strong temperature dependence is explained on the basis of carrier trapping by closely spaced impurity centers. Some measurements were made at lower frequencies. The results are consistent with the interpretation.

I. INTRODUCTION

MICROWAVE conductivity in semiconductors has been measured for the purpose of determining the effective mass and relaxation time of carriers,[1,2] polarizability of neutral impurities,[2] and density of injected carriers.[3] In these measurements, samples of low resistivities were used. The work presented here deals with impurity conduction at microwave frequencies. Boron-doped p-type silicon has been studied using samples with impurity concentrations less than 2×10^{17} cm^{-3}.

Impurity conduction under dc conditions has been investigated by many authors[4] for various semiconductors. At low-impurity concentrations, the conduction

* Work supported by Signal Corps and U. S. Army Research Office.
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[1] T. S. Benedict and W. Shockley, Phys. Rev. **89**, 1152 (1953); Y. Klinger, *ibid.* **92**, 509 (1953).
[2] F. A. D'Altroy and H. Y. Fan, Phys. Rev. **94**, 1415 (1954).
[3] A. F. Gibson and J. W. Granville, J. Electron. **2**, 259 (1956).
[4] For bibliography see Ref. 6.