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# Study of the de Haas–van Alphen Effect in Dilute Aluminum-Based Alloys*

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The de Haas–van Alphen effect has been studied in dilute alloys (up to 1 at.%) of Zn, Si, Ge, Mg, and Ag in aluminum. Three sets of oscillations, similar to those observed in pure Al arising from the third-zone Fermi surface, have been seen in most of the alloys. The periods of the oscillations are in general different from those of pure Al. These changes have been compared with the detailed predictions of the rigid-band model, and excellent agreement is found. In addition, the effective masses associated with the oscillations are found to be unchanged from those of pure Al. The Dingle temperatures, and hence relaxation times, for the electrons on the third-zone surface have been measured, and the scattering is found to be isotropic within the experimental error.

## I. INTRODUCTION

THE electronic structure of alloys has been of great interest since Hume-Rothery introduced his rules[1] for the boundary compositions of alloy phases. He showed that the number of valence electrons per atom is an important parameter. In the study of the electronic structure of metals, the form of the Fermi surface is also found to be an important factor in the transport properties of a metal.[2]

In recent years, the de Haas–van Alphen (dHvA) effect, in which the magnetic susceptibility is found to be oscillatory and periodic in the reciprocal of the magnetic field $H$, has proved to be a valuable tool for the study of the Fermi surfaces of pure metals.[3–5] Onsager[6] and later Lifshitz and Kosevich[7] have found theoretically that the period $P$ of the oscillation (in $1/H$) is related to the extremal cross-sectional area $S_m$ in $k$ space and in a plane normal to $H$, through the expression

$$P=2\pi e/\hbar cS_m. \tag{1}$$

The dHvA experiments on simple metals have, in general, been in very good agreement with the calculations based on few OPW and pseudopotential models of the Fermi surface as used by Harrison,[8] for example. Such success leads one naturally to try the more difficult case of the metal alloy, since there is much theoretical interest in the electronic state of a disordered alloy. The theory will be briefly reviewed in a following section. Many experiments have been performed with the aim of testing the theories and to give some clarification of the nature of the electronic state of an alloy. The more common of these are the measurement of (1) the specific heat which should be related to the density of states at the Fermi surface[9]; (2) the nonoscillatory part of the magnetic susceptibility, also related to the density of states[9,10]; (3) the Knight shift, which is related theoretically to the density of the electrons at the nuclei in the metal[11]; (4) the transport properties of the alloys.[12] There seems to be, however, much ambiguity or even disagreement between experiments and their various interpretations.[13]

Some dHvA experiments have been performed using dilute alloys and intermetallic compounds.[14,15] The latter are in theory, though not in the experimental difficulties which they pose, similar to pure metals and will not be discussed further. The common difficulty in the dHvA experiments on alloys is the drastic reduction in signal amplitude caused by the reduced mean free path of the conduction electrons. Thus the concentration of the solute must be kept small, which in turn means that any changes will be small, and high accuracy will be required. Alternatively, it is hoped to study sections of the Fermi surface which are extremely sensitive to the concentration of the solute, and thus the accuracy does not have to be so great.

The earliest study is that of Shoenberg and Uddin[16] on dilute alloys of bismuth, in which very small sections of the Fermi surface were extremely sensitive to minute quantities of solute. The band structure of pure bismuth,

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[1] W. Hume-Rothery, *The Metallic State* (Oxford University Press, London, 1936), p. 328.

[2] A. B. Pippard, *The Dynamics of Conduction Electrons* (Gordon and Breach Science Publishers, Inc., New York, 1965).

[3] A. S. Joseph and A. C. Thorsen, Phys. Rev. Letters **13**, 9 (1964).

[4] D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.

[5] D. Shoenberg, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), Part B, p. 680.

[6] L. Onsager, Phil. Mag. **43**, 1006 (1952).

[7] I. M. Lifshitz and A. M. Kosevich, Zh. Eksperim. i Teor. Fiz. **29**, 730 (1955) [English transl.: Soviet Phys.—JETP **2**, 636 (1956)].

[8] W. A. Harrison, Phys. Rev. **118**, 1190 (1960); **131**, 2433 (1963).

[9] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936).

[10] E. N. Adams, Phys. Rev. **89**, 633 (1953).

[11] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 93.

[12] See, for instance, Proceedings of the Sheffield Conference on the Electronic Structures of Alloys, 1963 (unpublished).

[13] See, for example, B. A. Green, Phys. Rev. **144**, 528 (1966).

[14] A. Beck, J. P. Jan, W. B. Pearson, and J. M. Templeton, Phil. Mag. **8**, 351 (1963).

[15] J. P. Jan, W. B. Pearson, Y. Saito, M. Springford, and I. M. Templeton, Phil. Mag. **12**, 1271 (1965).

[16] D. Shoenberg and M. Z. Uddin, Proc. Roy. Soc. (London) **156A**, 701 (1936).

however, was not known accurately enough[17] to test the theory of alloying. Gunnerson[18] and Gold[19] have studied dilute aluminum alloys and dilute lead alloys, respectively, but both these investigations were rather brief and with low precision, and were designed to confirm certain features of the Fermi surface of the solvent metal.

In fact, Gunnerson's results for the alloys of aluminum[18] are in contradiction to those of the present study and the band structure of aluminum now accepted. It was thought that the high-frequency oscillations, the $\gamma$'s, were associated with the second-zone hole surface.[20] There is now much evidence to indicate that these oscillations are in fact associated with the third-zone electron surface.[21–24] Marcus[25] and later Higgins and Marcus[26,27] studied dilute alloys of zinc and were able to interpret their results, for the most part, in terms of the rigid-band theory discussed in the next section. Here again very small sections of the Fermi surface were studied. In contrast, King-Smith[28] and Shoenberg[29] have studied larger sections in dilute alloys of the noble metals. The pulsed-field method used, however, doesn ot lend itself to the high precision needed and the results are more qualitative than quantitative.

Since the dHvA in pure aluminum was being studied in detail in this laboratory[23,24] and a pseudopotential calculation had been made[21] which was in good agreement with experiment, we decided to study aluminum-based alloys.

## II. ALLOY THEORY

Only a brief review of the relevant theory will be given. The theoretical treatment of an alloy is more difficult than that of a pure metal since the potential experienced by an electron no longer possesses the symmetry of the crystal lattice. Thus the use of Bloch functions[30] to represent the electron wave functions is no longer strictly valid. The electrons would better be represented by wave packets, since there is now a finite lifetime for the occupation of a state.

### A. Rigid-Band Model

The rigid-band model (RBM) was first introduced by Jones[31] to explain the Hume-Rothery rules.[1] Jones assumed that the lack of periodicity on alloying had no effect on the band structure, which remained the same as that of the pure solvent metal. The Fermi energy and surface were assumed to be changed to accommodate the appropriate number of electrons in the conduction band. For the nontransition-metal alloys, the number of electrons contributed to the conduction band by an atom was assumed to be the number of $s$ and $p$ electrons outside a closed valence shell. (See Table I for the values assumed in the present study.) Despite many criticisms, the RBM has been applied to the interpretation of the results of other experiments, for instance, the specific heats and the magnetic susceptibility of alloys.

An early objection to the RBM was that of Mott.[32] Mott suggested that if an atom of the solute was placed in a crystal of a solvent and if the resulting charge on the solute ion was different from that on the solvent ions, then the electrons in the conduction band would move to screen this excess charge. Using the Thomas-Fermi approach, a simple calculation shows that the excess electron charge in the atomic cell surrounding the solute ion is almost exactly equal to the negative of the excess ion charge. This means that the electron density, and hence the Fermi energy, is virtually unaltered outside the atomic cell containing the solute atom.

More recently, Friedel[33] was able to reconcile these two apparently contradictory views. Using a perturbation approach, he reasoned that although the conduction electrons do screen the solute ions, and hence the Fermi energy remains unaltered with respect to the vacuum level, the energies of the conduction states in the whole crystal are lowered by the screening. To a first approximation the dependence of energy $E$ on the wave number $k$ for the conduction band is also unaltered in shape, and is bodily displaced in energy with respect to the Fermi energy. The shift of the Fermi energy relative to the bottom of the conduction band is the same as that of the RBM. Thus there is the same change in the density of the states and the dimensions of the Fermi surface as is given by the RBM. Hence the use of the RBM is still justified in the study of the Fermi surface. In applying this model to the case of Al with three conduction electrons per atom alloyed with Zn, which has two conduction electrons per atom, the Fermi energy measured relative to the bottom of the conduc-

TABLE I. Number of conduction electrons per atom assumed in calculations.

| Element | Al | Ag | Mg | Zn | Si | Ge |
|---|---|---|---|---|---|---|
| Number | 3 | 1 | 2 | 2 | 4 | 4 |

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[17] V. Heine, Proc. Phys. Soc. (London) **A69**, 505 (1956); **A69**, 513 (1956).

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

[19] A. V. Gold, Phil. Trans. Roy. Soc. London **A251**, 85 (1958).

[20] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).

[21] N. W. Ashcroft, Phil. Mag. **8**, 2055 (1963).

[22] E. P. Vol'skii, Zh. Eksperim. i Teor. Fiz. **46**, 123 (1964) [English transl.: Soviet Phys.—JETP **19**, 89 (1964)].

[23] C. O. Larson and W. L. Gordon, Phys. Letters **15**, 121 (1965).

[24] C. O. Larson and W. L. Gordon, Phys. Rev. **156**, 703 (1967).

[25] J. A. Marcus, Phys. Rev. **77**, 750 (1950).

[26] R. J. Higgins, J. A. Marcus, and P. H. Whitmore, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), Part B, p. 859.

[27] R. J. Higgins and J. A. Marcus, Phys. Rev. **141**, 553 (1966).

[28] P. E. King-Smith, Phil. Mag. **12**, 1123 (1965).

[29] D. Shoenberg, Phil. Mag. **5**, 105 (1960).

[30] F. Bloch, Z. Physik **52**, 555 (1928); see also Ref. 9.

[31] H. Jones, Proc. Roy. Soc. (London) **A144**, 225 (1934).

[32] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[33] J. Friedel, Advan. Phys. **3**, 446 (1954).

tion band would decrease. This would lead to a decrease in the size of the electron Fermi surfaces and an increase in the size of the hole surfaces. Thus from Eq. (1) the dHvA periods associated with the electron surfaces would increase, while there would be a decrease for the hole surfaces. Alloying Al with Ge, which has four conduction electrons per atom, would produce changes in the opposite direction to those in the *Al*–Zn alloy.

### B. Nonrigid-Band Theories

The most serious failure of the RBM is in its predictions for the changes in specific heats on alloying of the noble metals.[34–37] Although the various authors are not in complete agreement,[13] it appears that the RBM not only gives the wrong magnitude but also the wrong sign for the changes in the electronic specific heat. This has prompted various theoretical attempts to explain these discrepancies. Cohen and Heine[38] first proposed that the band gaps of the solvent metal were modified on alloying. It was suggested that such a modification would account for the change in the electronic specific heat of Cu on the addition of Zn.[34] Ziman,[39] however, made a calculation which showed that such a modification would lead to a change of specific heat in the same direction as that given by the RBM and in the opposite direction to that of the experiment.

Recently, Jones[40] made an attempt to explain the anomaly by assuming that alloying leads to an averaging of the densities of states close to the Fermi energy. With suitable assumptions of the detailed dependence of the density of states of the pure solvent upon energy, the experimental results could be explained. This explanation has not been borne out by more detailed calculations.[41,42]

### C. Theory of the dHvA Effect in Alloys

The theoretical treatment of the dHvA in alloys has not been carried beyond a consideration of the effects of the increased scattering of the conduction electrons on alloying. Dingle[43] was the first to include the effects of scattering which results in an effective temperature $X$ which has become known as the Dingle temperature and is related to the relaxation time $\tau$ of electrons on the Fermi surface by the expression[43]

$$X=\hbar/4\pi^2k\tau. \tag{2}$$

Thus, if we modify the expression of Lifshitz and Kosevich[7] for the torque $C$ exerted on a sample suspended in a magnetic field $H$, to include the effects of scattering, then

$$C=\left\{\frac{4(e\hbar/c)^{1/2}}{(2\pi)^{3/2}\hbar^3}\frac{\partial S_m}{\partial\theta}\left(\frac{\partial^2 S_m}{\partial P_z^2}\right)^{-1/2}\cos\left(\frac{\pi m^*}{m_0}\right)\right\}$$
$$\times kTH^{1/2}\frac{\exp[-2\pi^2k(T+X)/\beta H]}{1-\exp(-4\pi^2kT/\beta H)}$$
$$\times\sin\left[\frac{S_m}{e\hbar H/c}\mp\frac{\pi}{4}-2\pi\gamma\right], \tag{3}$$

where the symbols are defined as follows: $k$ is the Boltzmann constant; $S_m$ is the extremal cross section of the Fermi surface in momentum space in a plane perpendicular to $H$; $P_z$ is the momentum of electrons in the $H$ direction; $\theta$ is an angular coordinate in a plane perpendicular to the axis of suspension of the specimen; $m_0$ is the free electron mass; $\beta$ is $e\hbar/m^*c$; and $m^*$ is the effective electron mass. This is for the fundamental period; we have neglected the summation over harmonics.[7] Later treatments[44,45] of the effect of scattering on the dHvA effect have confirmed Dingle's result. Alloying has its greatest effect on the amplitude of the dHvA signals, while the periods are virtually unaffected by the scattering. The RBM has been assumed to apply to the dimensions of the Fermi surface which determine the periods.[44,45] Brailsford,[45] however, has pointed out that there is a discrepancy of a factor of 2 between the $\tau$ used by Dingle in most of his paper[43] and the normally accepted collision time $\tau$. The Eq. (2) contains the correct factor.

## III. EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure used have been described in detail previously[24,46,47] and will only be described briefly here. The measurements were made with a self-balancing torque magnetometer in magnetic fields up to 23 kG.

For most alloy compositions, crystal suspensions with the ⟨100⟩ and ⟨110⟩ axes vertical were studied. Thus, with the rotation axis of the magnet vertical, it was possible to study any field direction in the (100) and the (110) planes.

The magnetic field was varied so that its reciprocal changed in an approximately linear manner in time. In this way the dHvA oscillations were generated with a constant frequency in time. Either broad- or narrow-band filters could then be used to sort out the component frequencies.[24] This technique, however, was not so

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[34] B. W. Veal and J. A. Rayne, Phys. Rev. **130**, 2156 (1963).

[35] L. C. Clune and B. A. Green, Phys. Rev. **144**, 525 (1966).

[36] B. A. Green and A. A. Valladares, Phys. Rev. **142**, 379 (1966).

[37] G. L. Guthrie, Phys. Rev. **113**, 793 (1959).

[38] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[39] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[40] H. Jones, Phys. Rev. **134**, A958 (1964).

[41] H. Jones, Proc. Roy. Soc. (London) **A294**, 405 (1966).

[42] P. G. Dawber and R. E. Turner, Proc. Phys. Soc. (London) **88**, 217 (1966).

[43] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500 (1952); **A211**, 517 (1952).

[44] S. J. Williamson, S. Foner, and R. A. Smith, Phys. Rev. **136**, A1065 (1964).

[45] A. D. Brailsford, Phys. Rev. **149**, 456 (1966).

[46] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 489 (1962).

[47] C. O. Larson, thesis, Case Institute of Technology, 1965 (unpublished).

useful as in pure Al, since in the alloys the increased scattering caused the amplitude of the oscillations to decrease rapidly with decreasing field, as indicated by Eq. (3). Filtering became of no use when this decay became comparable with the decay of the filter transients or "ring." Thus the narrow-band filter could not be used in many cases and occasionally even the broad-band filter was unsuitable.

On the other hand, the increased scattering in the alloys could help somewhat in the sorting of the frequencies. At a given orientation of the magnetic field to the crystal axes in Al, several frequencies are observed to beat together. These frequencies have, in general, different effective masses, and thus if the scattering is the same for all frequencies (see Sec. V C), Eq. (3) shows that the amplitudes will be affected to a different extent. Hence the $\alpha$ oscillations[24] tend to dominate in the more concentrated alloys.

In addition, the increased scattering reduced the magnitude and effects of eddy currents. This allowed larger samples of the alloys to be used than in the case of pure Al.[24] These advantages did not, however, compensate for the decreased amplitude of signal from the alloys.

The inability to filter properly and the decreased signal necessitates that the period-versus-angle data be much less complete for each alloy than for the pure Al. In many cases, large amplitude oscillations were seen, but from the character of the wave form it was obvious that several frequencies were present. The analysis of these frequencies, however, was not possible because some of the frequencies died away in amplitude in the course of the field sweep, hence changing the character and even the dominance of the signal. In these cases, the approximate results have not been included in the results presented here.

## IV. SPECIMEN PREPARATION

In addition to the usual requirements of a sample for dHvA measurements,[2] that is, a single-crystal specimen, the fact that the metal is an alloy adds a further complication, namely, that the concentration of the solute should be uniform throughout the specimen. The reason is that the dHvA amplitude depends in an inverse exponential manner on the concentration of the solute due to scattering of the electrons by the solute atoms (see Sec. V C). Hence, if there is any inhomogeneity in the solute concentration, the resulting dHvA signal will be heavily weighted toward that of the more dilute sections of the crystal. A composition determination which samples a large part of crystal, e.g., chemical analysis, will give, however, only an average composition leading to erroneous conclusions. Thus much effort was put into trying to produce homogeneous crystals and into testing them for any inhomogeneities. The method of preparation finally adopted will be described.

The constituents were first weighed out after etching from 99.999% starting stock.[48]

They were then melted together under an inert atmosphere in a high-purity carbon crucible of an induction furnace. High-vapor-pressure materials such as Zn could be added after the Al had been melted. Chill casting into a water-cooled graphite mould was then used to prevent segregation of the solute which is likely to occur with slow cooling. A 0.5 at.% Zn in Al ingot so prepared was checked by surveying longitudinal and transverse sections with a movable aperture 1 mm in diam mounted on a G.E. x-ray fluorescent spectrometer. The inhomogeneity in the Zn concentration was found to be less than 2% of the average concentration.

For most dilute-alloy systems the solute is more soluble in the liquid than in the solid phase. Thus crystal growth by melting and subsequent solidification could lead to large inhomogeneities in the concentration of the solute unless many precautions are taken. Fortunately, however, Al and its alloys will grow crystals by the strain anneal process.[49] Here it is not necessary to remelt the ingots after preparing the alloy. Details of the method have been given by Roberts.[50] After recrystallization, specimens were spark-cut from the alloy ingot and orientated in the normal manner by the back-reflection Laue technique. The specimens, normally cubes 0.15 in. on a side, were mounted in a light spring holder, similar to that of Larson and Gordon,[24] and attached to the torsion balance via a long quartz rod.

Pieces of the crystal adjacent to the specimen were analyzed for gradients and average composition, normally by the G.E. fluorescent spectrometer. The composition of the *Al*–Zn alloys was determined by calibrating the instrument with several standard Al alloys obtained from the National Bureau of Standards.[51] In addition, gradients in the alloys with Ag, Ge, and Zn were looked for, using small-diameter (1 mm and 0.1 mm) sampling probes which could be scanned over the surface of the test piece. As a precaution against accidental Bragg reflections, which would give a spurious intensity reading, the surface of the test piece was mechanically worked with emery paper. For this reason the actual specimen was not used for these measurements. No gradients were thus detected in the strain annealed crystals. One trial crystal, however, grown by a rapid molten zone pass showed gradients of several percent of the average solute concentration. The dHvA results from this sample have not been included here.[52]

The alloys with Si and Mg could not be checked for

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[48] Starting stock: Ag(99.999%), Al(99.999%), Ge(99.999%), Zn(99.999%), Mg(99.99%), Si(99.999%), supplied by United Mineral and Chemical Corp., New York, N. Y.

[49] J. J. Gilman, *The Art and Science of Growing Crystals* (John Wiley & Sons, Inc., New York, 1963).

[50] D. A. Roberts, thesis, Case Institute of Technology, 1965 (unpublished).

[51] National Bureau of Standards Samples Nos. SA 2027-8, SS 7072-C-23, SSA 214-R-6, and SAC 1193-30.

[52] These results were included in Ref. 53.

gradients in the above manner because of the poor signal-to-background ratio for these long-wavelength characteristic x rays. Samples of these and the Ge and Ag alloys, for which there were no standard alloys readily available, were chemically analyzed by commercial laboratories.

## V. RESULTS AND DISCUSSION

In pure Al there are three sets of dHvA oscillations that have been seen using this apparatus.[23] These[53,24] show excellent agreement with the predictions of Ashcroft[21] for electron orbits on the 3rd-zone Fermi surface of Al. One set, $\gamma$, arises from orbits about the arms of the 3rd-zone surface represented in Fig. 1 centered at the points U and K of the Brillouin zone. The other two sets are attributed to orbits near the point W: $\alpha$ on the necks at the ends of the arms and $\beta$ on the junctions between pairs of these necks. Three similar sets of oscillations have been observed in most of the alloys. The results for the dHvA periods, effective masses, and the Dingle temperatures will be discussed separately.

### A. Periods

The three sets of periods in the alloys were each found to exhibit the same general angular dependence on the magnetic-field position in the (100) and (110) planes as does the corresponding set in pure Al. This similarity is illustrated in Fig. 2, where the data for the $\alpha$ and $\beta$ oscillations in the (110) plane for Al, *Al*-Ge, and *Al*-Zn $\frac{1}{2}$ (see Table II for details of composition of the samples measured) are plotted together. Because of the difficulties discussed in Sec. III, the data for the alloys is not so detailed as that for pure Al.

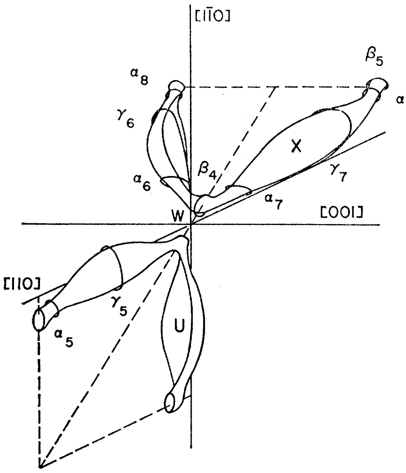

FIG. 1. The third-zone electron Fermi surface of Al, showing the three different types of orbit associated with the three sets of oscillations from Ref. 24.

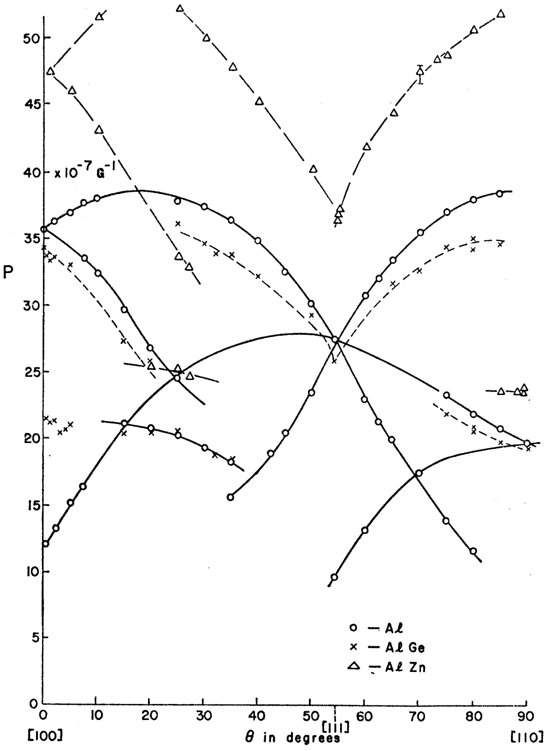

FIG. 2. A comparison of the dHvA effect in pure Al with that in *Al*-Zn $\frac{1}{2}$ and *Al*-Ge by a period-versus-orientation plot in the (110) plane for the $\alpha$ and $\beta$ oscillations.

As can be seen, however, the periods for *Al*-Zn $\frac{1}{2}$ are displaced from those of Al in the opposite direction to those of Ge. The changes observed are thus of the same sign as those predicted by the RBM, discussed in Sec. II A.

Larson and Gordon[23,24] found, for the $\alpha$ and $\gamma$ set of dHvA oscillations, that the product of effective mass and period at the same orientation of field was independent of the orientation within the accuracy of the experiment for a large range of field orientation. This lead us to consider the following idealized models of the portions of the Fermi surface giving rise to a set of oscillations. The extremal area $S_m$ may be described algebraically as a separable function of energy $E$ and angle $\theta$:

$$S_m = U(E)V(\theta). \tag{4}$$

Here the Fermi energy $E$ is measured from the bottom of the band and the field is at an angle $\theta$ from an arbitrary axis. Then, using Eqs. (1) and (4) and the relation[20]

$$m^* = \frac{\hbar^2}{2\pi}\frac{\partial S_m}{\partial E}, \tag{5}$$

we find that $m^*P \propto [\partial U(E)/\partial E]/U(E)$, which is a constant for a given Fermi energy. Here, $S_m$ is expressed in $k$ space.

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[53] J. P. G. Shepherd, C. O. Larson, D. A. Roberts, and W. L. Gordon, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), Part B, p. 752.

TABLE II. Alloy compositions and average period ratios.

| Sample | Composition at.% solute | Suspension | $P_0/P_c$ $\alpha$ | Limits | $P_0/P_c$ $\beta$ | Limits | $P_0/P_c$ $\gamma$ | Limits |
|---|---|---|---|---|---|---|---|---|
| *Al*Ge | 0.18 Ge | [100] | 1.058 | 1.062<br>1.053 | 1.025 | 1.036<br>1.010 | U.M.[a] | |
| | | [110] | 1.068 | 1.087<br>1.032 | 1.017 | 1.032<br>0.995 | U.M. | |
| | | Mean | 1.064 | 1.087<br>1.036 | 1.021 | 1.036<br>1.009 | U.M. | |
| *Al*Si II | 0.15 Si | [110] | 1.065 | 1.086<br>1.041 | 1.041 | 1.058<br>1.011 | U.M. | |
| *Al*ZnGe | 0.10 Ge | [100] | 0.999 | 1.017<br>0.976 | 0.991 | 1.020<br>0.955 | 0.998 | 1.003<br>0.996 |
| (Pseudo Al) | 0.10 Zn | [110] | 0.998 | 1.01<br>0.99 | 0.974 | 0.993<br>0.955 | U.M. | |
| | | Mean | 0.999 | 1.013<br>0.983 | 0.982 | 1.005<br>0.955 | 0.998 | 1.003<br>0.996 |
| *Al*-Zn $\frac{1}{4}$ | 0.258 Zn | [110] | 0.883 | 0.896<br>0.873 | 0.912 | 0.925<br>0.892 | 0.976 | 0.985<br>0.966 |
| *Al*-Zn $\frac{1}{2}$ | 0.507 Zn | [110] | 0.748 | 0.762<br>0.735 | 0.829 | 0.843<br>0.816 | 0.963 | 0.968<br>0.957 |
| *Al*-Zn II | 0.512 Zn | [100] | 0.776 | 0.797<br>0.741 | 0.845 | 0.871<br>0.837 | 0.969 | 0.980<br>0.957 |
| *Al*-Zn VI | 0.784 Zn | [100] | 0.604 | 0.616<br>0.599 | 0.752 | 0.758<br>0.742 | 0.950 | 0.948<br>0.952 |
| | | [110] | 0.615 | 0.628<br>0.596 | 0.767 | 0.776<br>0.759 | U.M. | |
| | | Mean | 0.610 | 0.675<br>0.598 | 0.756 | 0.770<br>0.742 | 0.950 | |
| *Al*-Zn V | 1.015 Zn | [100] | U.M. | | 0.730 | 0.747<br>0.717 | 0.922 | 0.944<br>0.908 |
| | | [110] | 0.482 | 0.493<br>0.468 | 0.684 | 0.714<br>0.658 | U.M. | U.M. |
| | | Mean | 0.482 | 0.493<br>0.468 | 0.714 | 0.747<br>0.667 | 0.922 | U.M. |
| *Al*-Ag | 0.09 Ag | [100] | 0.933 | 0.955<br>0.915 | 0.957 | 0.970<br>0.937 | | |
| | | [110] | 0.935 | 0.948<br>0.917 | 0.930 | 0.947<br>0.918 | 0.984 | 0.990<br>0.971 |
| | | Mean | 0.934 | 0.948<br>0.916 | 0.947 | 0.967<br>0.923 | 0.984 | 0.971 |
| *Al*Mg | 0.60 Mg | [110] | U.M. | | 0.834 | 0.851<br>0.826 | U.M. | |

[a] U.M. means unmeasureable.

If one makes the assumption that $V(\theta)$ is unchanged in alloying (i.e., the band structure is not disturbed, following the RBM), then from Eqs. (1) and (4) we find

$$\frac{P_0}{P_c}=\frac{S_c}{S_0}=\frac{U(E_c)}{U(E_0)}. \tag{6}$$

Thus, on comparing periods $P_c$ in the alloy with those of the pure solvent $P_0$ at the same orientation, the model predicts that the ratio is a constant independent of orientation.

To show the validity of Eq. (6), we plot in Fig. 3 the $\alpha$ periods of *Al*-Zn $\frac{1}{2}$ against the corresponding period of pure Al for various orientations. The choice of which period in Al to compare with an alloy period has been guided by similarities in the rotation diagram and relative amplitudes as compared with the other periods for the same sample. It is seen that the ratio is constant to a high degree and is found to be so for the other alloys. The dashed and full lines in Fig. 3 refer to theoretical calculations discussed below.

We shall present the results from the eight compositions, two orientations, and three sets of periods in the following convenient manner for clarity and will subsequently show the usefulness of this method in comparing the results with the RBM. For a given alloy, the

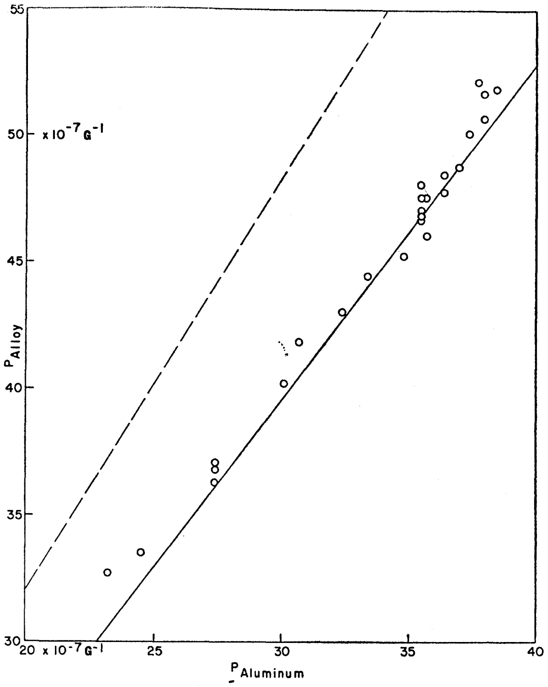

FIG. 3. A plot of the $\alpha$ periods observed in *Al*-Zn $\frac{1}{2}$ against the corresponding period in pure Al. In this and the three following figures, the full lines are computed, as explained in the text, using band-structure masses, while the dashed lines are computed using observed cyclotron masses.

ratio of $P_{\text{Al}}/P_{\text{alloy}}=S_c/S_0$ has been calculated for every period measured at the appropriate orientation. The mean value of this ratio has been tabulated in Table II, together with the limits of the range which contained 75% of all values of this ratio measured, for each suspension and for each sample measured.

It appears that in some cases, e.g., *Al*-Ge or *Al*-Ag, there is a small difference in value between two suspensions. It is thought, however, that this is due to the different dominance and ease of sorting of the $\alpha$ and $\beta$ periods for the two orientations. Thus the (100) plane is more suitable for measuring the $\beta$'s, while the (110) is better for the $\alpha$'s. The comparison of samples *Al*-Zn II (100) and *Al*-Zn (110), however, is very encouraging as a test of the over-all accuracy of the experiment, since these alloys were prepared about a year apart. Therefore, we have combined the results from both orientations, where available, for each alloy. These values are shown in Table II and have been plotted against the number of electrons per atom, calculated in the manner described in Sec. II A, in Figs. 4–6 for the $\alpha$, $\beta$, and $\gamma$ periods, respectively. The error bars represent the limits of the 75% range. They are not meant to be a measure of the absolute error of the experiment, although they are a general indication of the combined experimental errors together with the uncertainties connected with the assumptions in Eq. (6).

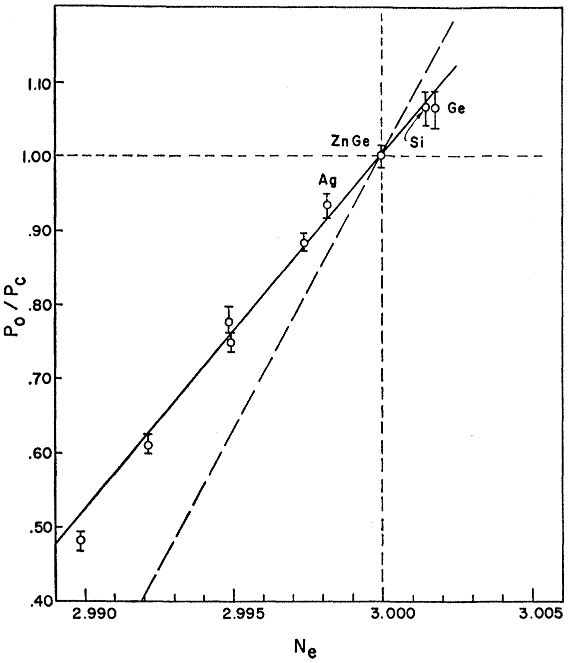

FIG. 4. The average-period ratio plotted against the electron-per-atom ratio for the alloys: the $\alpha$ oscillations. Data for solutes other than Zn are marked in this and in the following two figures.

There are obvious advantages in this method of treatment. Systematic errors at a particular orientation, due, for example, to the interference of other periods, are randomized. The main disadvantage is, of course, the suppression of any angular dependence of the ratio that may be present. It is thought, however, that if such an

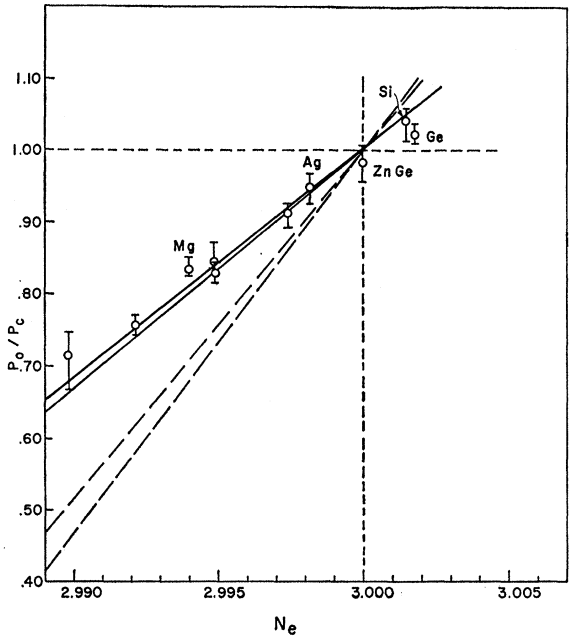

FIG. 5. Average-period ratio against electron-per-atom ratio: the $\beta$ oscillations. Here the upper line of each pair corresponds to the (100) data.

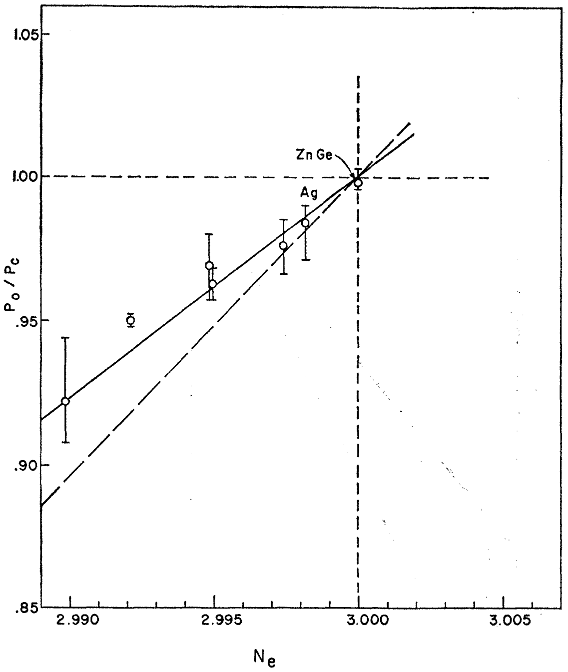

FIG. 6. Average-period ratio against electron-per-atom ratio: the $\gamma$ oscillations.

effect is present, the presence of systematic and other errors in the present method of measurement are sufficient to mask it, and we are unable to detect such a variation. It should be noted from Table II and Figs. 4–6 that for the *Al*-Mg alloy only $\beta$ oscillations were observed. The period of these oscillations agrees quite well with what would be expected from a comparison with the *Al*-Zn alloys. Possible causes for the nonobservance of the $\alpha$ and $\gamma$ oscillations are discussed later, in Sec. V C. The $\gamma$ oscillations were of very low amplitude in the alloys containing Si and Ge, and only in *Al*-Zn-Ge could they be measured. These low amplitudes are also discussed in Sec. V C.

The value of the period ratio, Eq. (6), can be calculated simply for each alloy since $S_c/S_0 = 1+(2\pi m^*/\hbar^2 S_0)\delta E_f$ [from Eq. (5)]. The change of Fermi energy is calculated from the change in the number of conduction electrons, assuming that each atom gives the number in Table I to the conduction band, and from the density of states. For Al this is taken to be the same as a free-electron sphere containing three electrons per atom.[21]

In addition to the change in the number of electrons, the change in lattice constants on alloying must also be considered. In calculating the effect of the latter on the dHvA periods, Shepherd *et al.*[54] made the following error. A calculation of the Fermi energy for a free-electron sphere, in which both the number of electrons per atom and the atomic volume are changed, will yield the change in the Fermi energy with respect to the original Fermi energy. In Al, however, the energy of the bottom of the third band will be changed by the change in the volume per atom. This can be seen by considering the unperturbed energy of any of the points on the Brillouin-zone faces. Thus, if we are to calculate the change in the dHvA period from Eq. (5) correctly, we must first measure the change of Fermi energy with respect to the bottom of the band. Thus the change in lattice constants is found to have negligible effect[55] and removes completely the 10% discrepancy reported earlier by Shepherd *et al.*[54] Here we have assumed that the change in lattice constants on alloying at helium temperatures is the same percentage as it is at 20°C.[56] This low sensitivity to changes in lattice constants is consistent with the work of Melz[57] on the pressure dependence of the $\gamma$ oscillations.

There are two possible choices for the cyclotron mass $m^*$ to be used in this calculation: the observed value or a band-structure value. In Figs. 3–6, the full lines represent the calculations using Ashcroft's band-structure masses,[21] while the dashed lines involved the use of the experimentally measured effective masses (see Sec. V B). The lines are doubled in the case of the $\beta$ results in Fig. 5 since the mass period product approximation does not work well for this set. The masses at (100) and (110) have been used for the two lines.

The agreement of the experimental points with the calculations involving Ashcroft's band-structure masses is seen to be very good in all three cases. This shows that the RBM is a good description of the band structure of Al on alloying. In addition, the agreement with the band-structure masses rather than the experimentally measured masses suggests that the later are enhanced[23] in Al by approximately 40%. It is not surprising that the agreement is better for the band-structure masses since the cyclotron mass as observed in the dHvA effect should be enhanced by an electron-phonon interaction[58]

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[54] J. P. G. Shepherd, D. Roberts, and W. L. Gordon, Phys. Letters **18**, 103 (1965).

[55] On a free-electron model (Ref. 9) the Fermi energy is given by the relation $E_f = K(n/V_a)^{2/3}$, where $n$ is the number of electrons per atom, $V_a$ is the atomic volume, and $K$ is a constant. Thus we get from partial differentiation

$$\frac{\delta E_f}{E_f} = \frac{2}{3}\frac{\delta n}{n} - \frac{2}{3}\frac{\delta V_a}{V_a}.$$

The energy of the bottom of the band, taken as a point on the Brillouin-zone face, is given by the relation

$$E_b = C(2\pi/a)^2,$$

where $a$ is a lattice constant and $C$ is a constant of proportionality. Thus $\delta E_b/E_b = -2\delta_a/a$, but $\delta V_a/V_a = 3\delta a/a$. Hence the change of Fermi energy relative to the bottom of the band is

$$\delta E_f - \delta E_b = \frac{2}{3}E_f\frac{\delta n}{n} - \frac{2}{3}\frac{\delta a}{a}(E_f - E_b).$$

Thus for a small band where the Fermi energy is close to the bottom of the band, $E_f \simeq E_b$, and thus the effect of the lattice constants is negligible.

[56] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Ltd., London, 1958).

[57] P. J. Melz, Phys. Rev. **152**, 540 (1966).

[58] J. W. Wilkins and J. W. F. Woo, Phys. Letters **17**, 89 (1965).

which changes the bands very close to the Fermi energy but does not alter the over-all shape of the bands. [To predict the change with solute concentration, we have used the relation $\delta S=(\partial S/\partial E)(\partial E/\partial n)\delta n$. We assume that $\partial E/\partial n$ is free-electron-like from the general band structure of Al and is not influenced by enhancement.[59]]

The full lines in Figs. 4–6 cross the zero-cross-section axes at the following approximate values of electron-per-atom ratio $N_e$: 2.980 for the $\alpha$ oscillations, 2.967 for the $\beta$'s, and 2.870 for the $\gamma$'s. If the above theory holds for such large concentrations of solute, then the third-zone arms of the Al Fermi surface would be expected to separate at about 2–4 at.% Zn and to disappear completely at about 13 at.% Zn. There is considerable uncertainty in the first value since the arms will pinch off near the point W, where the $\alpha$ and $\beta$ cross sections are situated. The complication arises from the region of the third zone that produces the $\beta$ oscillations, since in Ashcroft's model this region is not described by a simple parabolic band characterized by a single effective mass, but by the crossing of two bands. Therefore, the lines in Fig. 5 which are calculated for a simple band using Ashcroft's masses will not be a good description close to the crossing point. Such changes in the connectivity of the Fermi surface would be expected to show some effect on the transport properties of the alloys of Al. Matsuda and Sato[60] have studied the Hall effect in Al alloys and attributed a discontinuity in the slope of the Hall coefficient at an $N_e$ of 2.95 as being due to some Fermi-surface effect such as a "pinching off" of the third-zone arms. This interpretation is not in contradiction to the above considerations. Yurkov *et al.*[61] have studied the thermopower in Al alloys. They find some changes in slope near an $N_e$ of 2.85. This could be attributed to the disappearance of the third-zone electrons.

The criticism may be made that we are drawing rather general conclusions for the whole of the Fermi surface when in fact we have only made observations on a small part of the surface and have not made any measurements on the large second-zone hole surface. Since, however, the second-zone surface has a much greater (approximately 10 times) density of states than the third-zone surface, any change of the hole band relative to the electron band would be strongly reflected in changes in the Fermi surface of the latter, via changes in the common Fermi energy. Thus, since the changes in the third-zone surface are consistent with the RBM, it can be assumed the changes in the hole surface are also consistent. Of course, changes in the second-zone band could be imagined such that the Fermi energy would not be altered in a way inconsistent with the RBM. This, however, would require that the change in the *total* number of states below the Fermi energy be the same as that predicted by the RBM. Although not impossible, this is thought to be unlikely. It was thought, however, that it would be interesting to know how the specific heat of Al changed on alloying since this should measure the density of states at the Fermi surface. Green and Dicke of this university kindly agreed to make such measurements on samples prepared by us. The results[62] show qualitatively RBM behavior unlike that found in a previous investigation,[63] in that the electronic specific heat increases on alloying with Ge and decreases on alloying with Zn. Quantitatively, however, the agreement is not good, since the rate of change with $N_e$ is about three times that expected from the RBM. The reason for this discrepancy is not understood.

We still feel that the RBM is a good description of the changes in the electronic state of Al on alloying.

### B. Effective Masses

Effective masses of the electrons producing the dHvA oscillations were measured in the conventional manner by determining the temperature dependence of the amplitude of the oscillation concerned. This method has been discussed in detail by Larson and Gordon,[23,24] particularly in respect of the errors present and the precautions necessary when filtering. Because of the difficulties in separating the contributions of the different oscillations, masses were measured at only a few representative orientations and filtering was not used. The results are presented in Table III, together with the values for pure Al. As can be seen, there is no significant change on alloying. The accuracy of the measurements

TABLE III. Cyclotron masses measured in alloys and in Al[a] at the same orientation.

| Sample | Suspension | Orientation with respect to [100] | Set | Alloy $m^*/m$ | Al $m^*/m$ |
|---|---|---|---|---|---|
| *Al*ZnGe | [100] | 0.5° | $\alpha$ | 0.091 | 0.091 |
| *Al*Zn II | [100] | 0.5° | $\alpha$ | 0.091 | 0.091 |
| *Al*Zn VI | [100] | 0.5° | $\alpha$ | 0.085 | 0.091 |
| *Al*Zn $\frac{1}{2}$ | [110] | 0.2° | $\alpha$ | 0.088 | 0.091 |
| *Al*Ge | [100] | 44.9° | $\alpha$ | 0.114 | 0.118 |
| *Al*ZnGe | [110] | 89.9° | $\alpha\beta$ | 0.118 | 0.119 |
| *Al*Zn $\frac{1}{4}$ | [110] | 89.9° | $\alpha\beta$ | 0.120 | 0.119 |
| *Al*Zn $\frac{1}{2}$ | [110] | 89.9° | $\alpha\beta$ | 0.115 | 0.119 |
| *Al*Si II | [110] | 89.9° | $\alpha\beta$ | 0.109 | 0.119 |
| *Al*Ge | [110] | 89.9° | $\alpha\beta$ | 0.118 | 0.119 |
| *Al*ZnGe | [110] | 70.0° | $\alpha$ | 0.091 | 0.091 |
| *Al*Zn $\frac{1}{2}$ | [110] | 70.0° | $\alpha$ | 0.091 | 0.091 |
| *Al*Zn II | [100] | 0.1° | $\gamma$ | 0.177 | 0.180 |
| *Al*Zn $\frac{1}{2}$ | [110] | 0.1° | $\gamma$ | 0.175 | 0.180 |
| *Al*Zn II | [100] | 40.0° | $\gamma$ | 0.128 | 0.131 |
| *Al*Zn $\frac{1}{2}$ | [110] | 54.5° | $\gamma$ | 0.159 | 0.150 |
| *Al*Zn $\frac{1}{2}$ | [110] | 62.5° | $\gamma$ | 0.162<br>0.145 | 0.160<br>0.141[b] |

[a] References 23, 24.
[b] From $m^*P$ product.

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[59] R. E. Prange and L. P. Kadanoff, Phys. Rev. **134**, A566 (1964).

[60] T. Matsuda and T. Sato, J. Phys. Soc. Japan **21**, 1494 (1966).

[61] V. A. Yurkov, N. A. Dutysheva, and L. B. Okolykhina, Fiz. Metal. i Metalloved. **20**, 512 (1965).

[62] D. A. Dicke and B. A. Green, Phys. Rev. **153**, 800 (1967).

[63] H. J. Blythe, T. M. Holden, M. Dixon, and F. E. Hoare, Phil. Mag. **11**, 235 (1965).

is not better than 3%. This constancy of the effective masses is in agreement with the RBM.

### C. Dingle Temperature and Scattering

Initially, the Dingle temperatures were determined in the conventional manner by measuring the field dependence of the amplitude of the oscillations at a constant temperature.[4,23] Results obtained in this way for the $\alpha$ and $\gamma$ oscillations in the *Al*-Zn alloys for an orientation of 70° from the [100] axis in the (110) plane are shown in Fig. 7. According to these results, it would appear that *Al*-Zn $\frac{1}{4}$ had a larger Dingle temperature or greater scattering than *Al*-Zn $\frac{1}{2}$, which is not to be expected from the composition of the alloys. It was found, however, that more consistent results were obtained in the following manner. The absolute amplitude $C$ at a particular field $H$ was measured and normalized by dividing by the mass of the sample. The difference in Dingle temperature $\delta X$ between two samples for a given period and orientation can be found by using the following equation derived from Eq. (3):

$$X_1-X_2=\frac{HK}{(m^*/m)}\ln(C_2/C_1), \qquad (7)$$

where $K=(e\hbar/mc)(1/2\pi^2k)$, where $C_1$ and $C_2$ are the normalized amplitudes of the two samples. This is for measurements made at the same temperature and

$$X_1-X_2=T_2-T_1+\frac{HK}{(m^*/m)}\ln(C_2T_1/C_1T_2) \qquad (8)$$

for measurements made at different temperatures, where the factor $\exp(-T/HK)\ll 1$. The subscripts refer to the two samples in question. In the derivation of Eqs. (7) and (8) we have made the assumption that the terms in curly brackets in Eq. (3) remain the same on alloying.

We have measured this difference in Dingle temperature between Al and as many of the samples as possible. In some cases, we have only been able to put a lower limit on this difference, where the amplitude of the signal from one of the samples was too small to measure. By comparing every sample with Al and assigning a Dingle temperature of 0.7°K to Al, as that measured by Larson,[47] we can arrive at a value for the Dingle temperature for each sample. In Fig. 7, we compare the results for the *Al*-Zn series with those of the conventional method.

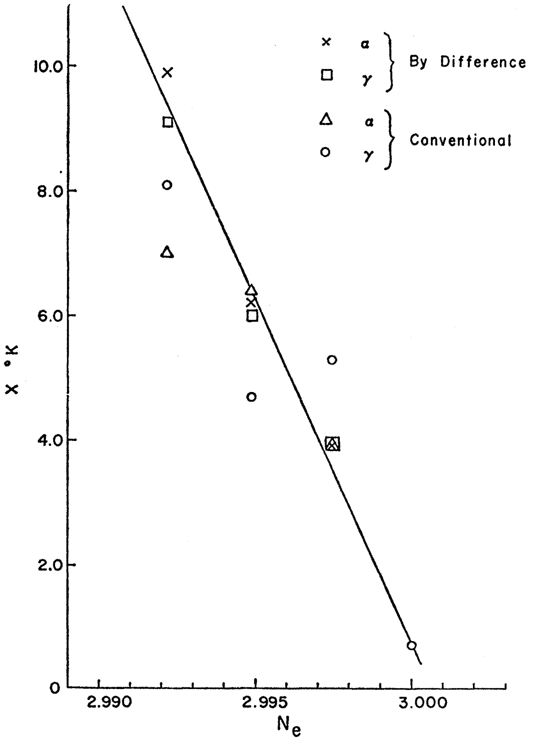

FIG. 7. A comparison of the conventional and difference method for the Dingle temperature $X$ by a plot of $X$ against electron-per-atom ratio for the $\alpha$ and $\gamma$ oscillations at 70° in (110) plane for the *Al*-Zn alloys. The point at 3.00 (pure Al) was obtained from Ref. 47.

It is of interest[64] to see if the scattering of electrons is isotropic over the Fermi surface of the metal. The dHvA effect provides a direct experimental test of this. To this end, we determined the Dingle temperatures of the alloy specimens at as many different orientations as possible. The results are presented in Table IV and in Fig. 8. In the calculations the effective masses of pure Al[23] were used, interpolating with the constant mass-period product where necessary. In Fig. 8, a comparison is also made between the influence of electron scattering on the dHvA effect and on resistivity. The incremental Dingle temperature for each alloy, $X$, is divided by $X_T$, computed from a resistivity relaxation time in the single-band model:

$$\sigma=Ne^2\tau/m. \qquad (9)$$

Resistance ratios $R_{273^\circ\mathrm{K}}/R_{4.2^\circ\mathrm{K}}$ obtained from our own alloys were used in this calculation and are shown in Table IV. The change in N with alloying was neglected and the free-electron mass used.[59] The resistance ratios that were not measured were obtained by interpolation from the other *Al*-Zn alloys and were found to be consistent with resistivity data.[65] The scattering appears to be isotropic over the third zone. Furthermore, close agreement of the measured Dingle temperatures with those calculated from bulk measurements, which are dominated by the scattering of the majority second-zone carriers, would indicate that the scattering is approximately isotropic over the entire Fermi surface. This is somewhat surprising, since one would expect the dHvA amplitude to be more sensitive to small-angle scattering than the conductivity, and thus the measured Dingle temperature would be expected to be much greater than that calculated in such a simple manner as indicated above. Of course, since we could not observe

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[64] V. Heine, Phil. Mag. **12**, 53 (1965).

[65] W. L. Fink and L. A. Willey, Trans. AIME **122**, 244 (1936).

TABLE IV. Dingle temperature of the alloys calculated using the difference method.[a]

| Orientation with respect to [100] | Suspension | Set | *Al*Zn $\frac{1}{4}$ | *Al*Zn $\frac{1}{2}$ | *Al*Zn II | *Al*Zn VI | *Al*Zn V | *Al*ZnGe | *Al*Ge | *Al*Si II | *Al*Ag |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1° | [110] | $\alpha$ | 3.9 | 6.6 | | 10.3 | | 8.0 | 7.5 | 8.5 | 6.2 |
| 40° | [110] | $\alpha$ | 3.6 | 5.8 | | 9.0 | | 5.4 | 7.4 | 8.5 | 6.4 |
| 70° | [110] | $\alpha$ | 3.9 | 6.2 | | 9.9 | >12 | 5.4 | 8.1 | 9.0 | 6.5 |
| 1° | [100] | $\alpha$ | | | | 9.3* | | 6.2* | 7.2* | | |
| 15° | [100] | $\alpha$ | | | | 11.2* | | | | | 9.2* |
| 44° | [100] | $\alpha\beta$ | | | | | | 6.7* | 7.6* | | 7.8* |
| 85° | [110] | $\beta$ | 3.3 | 5.6 | | 8.0 | >9.9 | 5.4 | 6.3 | 7.3 | 6.0 |
| 10° | [110] | $\gamma$ | 3.4 | 6.8 | | | | | | | 5.9 |
| 30° | [110] | $\gamma$ | 3.9 | 6.4 | | | | | | | |
| 70° | [110] | $\gamma$ | 3.9 | 6.0 | | 9.1 | | 9.2 | >12.3 | | 6.5 |
| 1° | [100] | $\gamma$ | | | | | | 7.7* | | | |
| 15° | [100] | $\gamma$ | | | | 11.0* | | | | | 7.1* |
| R(273°K)/R(4.2°K) | | | 54 | | 29 | | | 29 | 18.2 | 19.5 | 31 |

[a] These values are referenced to Al assuming a D.T. of 0.7°K except those marked *, which are referenced to Al Zn II assuming D.T. of 6.2°K.

the oscillations corresponding to the second-zone surface, it is quite possible that the Dingle temperature for these oscillations could be much higher than that of the third zone. It should be noted that even if these oscillations were observed by us, the determination of a Dingle temperature would be very difficult since these oscillations would be extremely sensitive to microstructure.[66] Following Brailsford,[45] we have calculated the ratio $X/X_t$ for isotropic scattering by a Thomas-Fermi potential. For Al we calculate $X/X_t=1.7$. As can be seen from Fig. 8, the agreement is not very good. We do not intend to discuss the possible reasons for the inconsistency here.[67]

### D. Discussion of the Experimental Determination of Dingle Temperatures

The conventional method for determining the Dingle temperature seems to give less consistent results than the difference method. Even more extreme examples than those quoted above have been found in this laboratory. Some reasons for these discrepancies are now proposed. (1) In certain cases, e.g., the $\alpha$ and the $\gamma$ oscillations near the $\langle 100\rangle$ and the $\langle 110\rangle$ axes, a misorientation of the axis of suspension can cause a single oscillation to split into two oscillations of slightly different period. These two periods will then beat together. If the difference is slight, the period of the beat will be very large and the normal decay of amplitude with field can mask this, so that it is not obvious that such a beat is present. The beat, however, will change the field dependence of the amplitude of the oscillations and can lead to an increase or a decrease of the Dingle temperature. Thus a simple calculation shows that a 1° misorientation in the axis of suspension could lead to a maximum error of ±2°K for the $\alpha$ oscillations. The beat period, however, would be 50 oscillations long, and since, in the experiments described here, only about 10–15 oscillations were observed in the range 23–10 kG, it would be difficult to detect. (2) Microstructure in the sample can lead to a reduction of amplitude, as pointed out by Priestly.[66] This reduction of amplitude is field-dependent, however, and hence can lead to an increase in the decay of amplitude and hence an increase in the Dingle temperature. The reduction of amplitude is[66] given by

$$A/A_0=\exp[\pi ab/P_0H]^2, \qquad (10)$$

where $a=(1/P)\partial P/\partial\theta$, and $b$ is the half-width of the

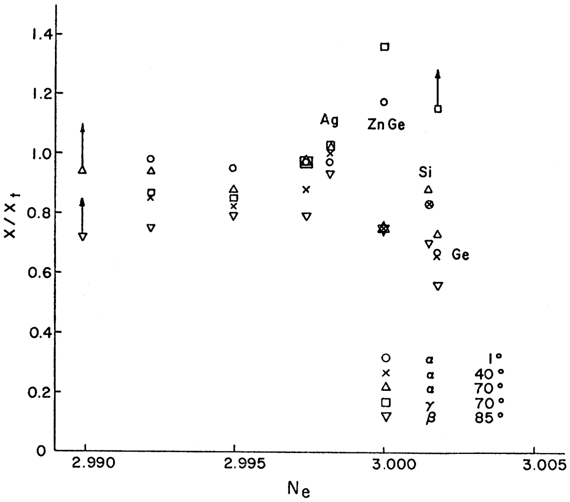

FIG. 8. Comparison of Dingle temperatures, determined by the difference method, at different orientations for each alloy with a "Dingle temperature" estimated from resistivity data. Arrows indicate that the ratio may be greater than the data point shown.

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[66] M. G. Priestley, Phil. Mag. 7, 1205 (1962).

[67] Although the transport properties are not expected to be affected by the electron-phonon enhancement due to a cancellation of terms (Ref. 59), it can be argued that the relaxation time could be changed. Thus a value of $m=1.4m_0$ should be used in Eq. (9), which would give better agreement between Fig. 8 and the calculated value of $X/X_t=1.7$.

Gaussian spread of orientations in the sample. This factor can cause very large errors, especially in the oscillations with the smaller periods (e.g., the $\gamma$'s). (3) Another distinct period may be present, and this could have an effect on the amplitude in several ways. The second period could decay away rapidly or it could beat in different ways through the field sweep.

The difference method of determining the Dingle temperature is of course affected by these three effects. It is affected, however, to a much smaller extent than the conventional method. For example, an error of as much as 50% (due to the above causes) in the amplitude of the $\gamma$ oscillations at a field of 23 kG leads to an error in the DT of only $\frac{1}{2}$°K. Errors in the amplitude as large as this in the conventional method would lead to a much larger error in the Dingle temperature.

It is believed by the authors that microstructure is the reason that only the $\beta$ oscillations were observed in the *Al*-Mg sample. The angular dependence of the $\alpha$ and $\gamma$ oscillations is much greater than that of the $\beta$'s, and hence from Eq. (10) it can be seen that their amplitudes will be more greatly reduced. Large single crystals of *Al*-Mg alloys were very difficult to grow and several abortive attempts were made before a sample large enough to measure was obtained. This is in contrast to the *Al*-Zn crystals, which were very easily grown. In addition, resistivity measurements[68] would lead one to expect that there would be less scattering in the *Al*-Mg alloys than in the *Al*-Zn alloys. The signals from the *Al*-Zn samples were much larger, however, and the resistance ratio of our alloys correspondingly high. The reason for this unusual behavior of the *Al*-Mg alloys on crystallizing is not known.

Evidence against the microstructure hypothesis is that of the Laue back-reflection photographs, which showed that the diffraction spots from the *Al*-Mg sample were no more diffuse than those of the other samples. This was a spot size of less than 1°, while a calculation based on Eq. (10) would indicate that a spread of 2°–3° was necessary to cause the amplitude of the $\alpha$ and $\gamma$ oscillations to be reduced to an unobservable magnitude. The x rays, however, only penetrate the crystal to a depth of a few tenths of a millimeter and perhaps the microstructure lies deeper than this or the crystallites were larger in size than this.

Microstructure could also be the cause of the low amplitude of the $\gamma$ oscillations and an increase in the $\beta$'s relative to the $\alpha$'s in alloys containing Si and Ge. It is possible, however, in all these alloys that the scattering is highly dependent on the part of the Fermi surface that the scattered-electron state occupies. For the *Al*-Zn alloys there does not seem to be this doubt, however, and the scattering appears to be isotropic.

## VI. SUMMARY

Measurements of the dHvA effect in Al-based alloys are in complete agreement with the rigid-band model when applied to the pseudopotential model of Ashcroft.[21] In addition, they suggest that the cyclotron effective mass is enhanced over the band-structure value.

The scattering as deduced from the change of amplitude of the oscillations on alloying appears to be isotropic over the third-zone Fermi surface, and it is deduced from the conductivity to be isotropic over the whole surface.

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