undergoing heating. Evidently some rate effect accounts for the differences in the two curves. An indication of the uncertainty in the values is given by the length of the lines through the points. In the low-pressure range (i.e., from atmospheric pressure to about 7 kbar), the Curie temperature appears to increase with increasing pressure. The shapes of the curves in Figs. 5 and 6 make a more precise determination difficult to obtain. In the high-pressure range (beyond 7 kbar), the Curie temperature appears to decrease with increasing pressure, having a coefficient of $-0.8°\mathrm{K}/(\mathrm{kbar})$.

ACKNOWLEDGMENT

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de Haas–van Alphen Effect and the Fermi Surface of Dilute Alloys of Zinc*

R. J. Higgins†‡ and J. A. Marcus
Northwestern University, Evanston, Illinois

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Torsion measurements have been made of the de Haas–van Alphen magnetic-susceptibility oscillations in dilute Zn-Cu (up to 0.2 at.%) and Zn-Al (0.1%) alloys in magnetic fields up to 33kG. Sizeable alloying effects occur in the two longest periods P_1 and P_2 (the two smallest orbits on the zinc Fermi surface). Both periods *decrease* by 30% with only 0.2% Cu. With 0.1% Al, P_2 *increases* substantially while P_1 is only slightly increased, by an amount comparable to the 4% uncertainty in period determination (the oscillation amplitude is very small in the alloys). Following an earlier suggestion of Harrison, these alloying changes have been interpreted using the nearly-free-electron construction. The model explains both the sign and the magnitude of the P_1 changes, in particular demonstrating that the dominant effect of the axial-ratio change can make a metal of *lower* electron concentration act to *increase* the size of an electron piece of the Fermi surface. The model accounts for the sign but not the magnitude of the P_2 changes, which are more than a factor of three larger than predicted by the model. No changes greater than 1% were observed in the third longest period P_3. An unexplained result is the observation of a period of order $400\times10^{-7}\mathrm{G}^{-1}$ for fields in the (0001) plane in crystals containing copper impurities, but not in pure zinc or Zn-Al.

INTRODUCTION

An explanation for the regularity observed by Hume-Rothery in phase diagrams of the noble metals was suggested by Jones more than 30 years ago.[1] His explanation considers the effect of anomalies in the density of states which occur in the regions of electron concentration where the Fermi surface (FS) contacts a Brillouin-zone boundary. This concept has been used by Jones and others to interpret phase boundaries, and, in hexagonal metals, axial-ratio changes on alloying.[2,3] The starting point for all of these interpretations was a postulated FS whose topology could not be well verified experimentally or theoretically. This situation has changed with the advent of experimental techniques such as the de Haas–van Alphen (dHvA) effect for the experimental measurement of the FS.[4] The dHvA oscillations in magnetic susceptibility are observed in pure metals in high magnetic fields ($\omega_c\tau>1$, where $\omega_c=eH/m^*c$) at low temperatures ($kT<\hbar\omega_c$). The oscillations are periodic in inverse magnetic field $1/H$, with period inversely proportional to the extremal cross-sectional area A of the FS perpendicular to the magnetic-field direction[5]:

$$P=\Delta 1/H=2\pi e/\hbar cA \quad (A \text{ in } k \text{ space})\,. \tag{1}$$

With such measurements it has been found[6,7] that in the pure noble metals the FS contacts the (111) zone face. This is a major distortion of the free-electron sphere and throws into doubt the earlier explanation[1] that the α-phase boundary of the noble-metal alloys is due to (111) zone face contact at an electron/atom ratio of 1.4. Though attempts have been made to patch up the theory,[8] a more direct approach would be FS measure-

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† Part of a dissertation submitted to the Graduate School of Northwestern University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

‡ Present address: Department of Physics, University of Oregon, Eugene, Oregon. National Science Foundation predoctoral fellow while at Northwestern.

[1] A recent review has been given by W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (The Institute of Metals, London, 1962), pp. 310–340.

[2] T. B. Massalski and H. W. King, Progr. Mater. Sci. **10**, No. 1 (1961).

[3] T. B. Massalski and H. W. King, Acta. Met. **10**, 1171 (1962).

[4] See, for example, *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, New York, 1960).

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

[6] A. B. Pippard, Phil. Trans. Roy. Soc. **A250**, 325 (1958).

[7] D. Shoenberg, Phil. Trans. Roy. Soc. **A255**, 85 (1962).

[8] W. Hume-Rothery and D. J. Roaf, Phil. Mag. **6**, 55 (1961). See also Ref. 1, p. 329.

ments on alloys. The problem is that dHvA amplitudes become small owing to impurity scattering before changes in the FS (dHvA period) become appreciable.[9–12] Thus, only dilute alloys can be used, and only the smallest FS segments will show appreciable size changes.[13] Alloying size changes in these small FS segments will usually be orders of magnitude smaller than size changes in comparable segments in semimetals or semiconductors, since in metals the small segments must share the added electrons with the rest of the large FS.

We were encouraged to study alloys based on zinc rather than noble metals because of earlier experiments[14,15] which showed that the longest period dHvA oscillation in zinc was very sensitive to alloying, and that alloying did not completely destroy the amplitude of the oscillations (The upper-limit composition of 0.3% Cu was determined by the solubility limit,[16] not by the sensitivity of the apparatus). Though less theoretical attention has been paid to zinc alloys than to noble metal alloys, there is more hope for a simple understanding of alloying behavior of zinc than the noble metals because of ample experimental[17,18] and theoretical[19] evidence that pure zinc behaves as a nearly free-electron metal. Additional interest in FS measurements on alloys of zinc with monovalent metals comes from the recent lattice parameter measurements of Massalski and King.[3] In the vicinity of pure zinc there are *two* hcp phases with c/a ratios below and above the ideal close-packed value. It was suggested[3] that these two phases differ by a FS overlap, evidence coming from the observation of a sharp upturn in the c/a ratio of the ϵ phase ($c/a<$ideal) as the η phase ($c/a>$ideal) boundary is approached.

Alloying measurements will be interpreted using the nearly free electron (NFE) model of Harrison,[19,20] whose validity for pure zinc has been established experimentally.[17,18] Of most interest in this paper are a tiny needle-like segment of the FS containing about 10^{-6} electrons/atom, whose long axis is along the c axis of the crystal, and several small orbits (horizontal and diagonal arms) on a multiply connected hole segment (Fig. 1). It will be assumed that Cu or Al contributes one or three electrons per atom, respectively, to the NFEFS.

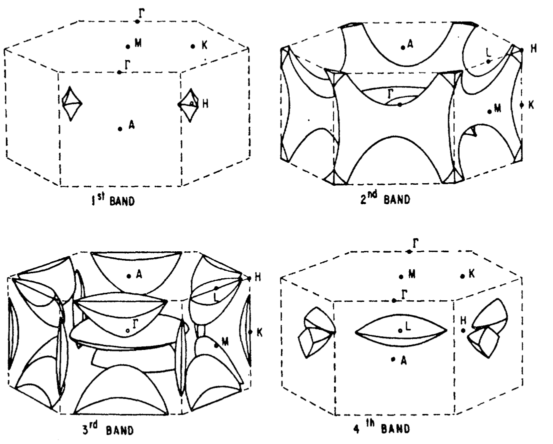

FIG. 1. The nearly free-electron Fermi surface for zinc (drawing taken from Ref. 19). The orbits of interest in this paper are on the needle-like segment in the 3rd band at K (dHvA oscillation referred to as P_1), the horizontal arm adjacent to the point M on the 2nd band segment (P_2), and, on the same segment, the diagonal arm connecting the central ring to the point H (P_3). For further discussion of the model and its relevance to dHvA observations on zinc, see Refs. 16, 18, and 19.

A method of interpreting the sign and magnitude of alloying changes has been suggested by Heine,[21] which makes use of the measured cycloton effective mass

$$m^*=(\hbar^2/2\pi)(\partial A/\partial E_F) \qquad (2)$$

to express the extremal area change to first order as

$$dA=(2\pi/\hbar^2)m^*dE_F \quad (m^*+\text{for electrons, }-\text{for holes})\,. \qquad (3)$$

The magnitude of the area change is therefore determined by the size of the measured effective mass, and the Fermi energy change on alloying, which Heine calculated on the basis of Friedel's theory of the screening radius. A calculation[22] based on this approach shows area changes for the needle FS segment (labeled P_1[18]) in zinc of nearly observed magnitude ***but of the wrong sign.*** The needle period is observed to decrease with Cu impurities, which with the Heine model indicates a hole segment, whereas Harrison's NFEFS model[20] shows P_1

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[9] J. S. Dhillon and D. Shoenberg, Phil. Trans. Roy. Soc. **A248**, 1 (1955).

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

[11] G. T. Croft, W. F. Love, and F. C. Nix, Phys. Rev. **95**, 1403 (1954). F. T. Hedgcock and W. B. Muir, *ibid.* **129**, 2045 (1963).

[12] A notable exception is the work of J. P. G. Shepherd, C. O. Larson, D. Roberts, and W. L. Gordon, *Proceedings of the Ninth International Conference on Low Temperature Physics, 1964* (Plenum Press, Inc., New York, 1965). Using a sensitive torsion balance, changes in the longer periods of up to 25% were observed in Al with up to 0.5% Zn.

[13] In the nearly free electron model, *fractional* size changes will go roughly as the circumference of the orbit over the area, or roughly as the square root of the period. In addition, small pieces of the FS are generally associated with low cyclotron effective mass, so that the observability criterion ($\omega_c\tau>1$) can be more easily achieved.

[14] J. A. Marcus, *Proceedings of the International Conference on Physics of Very Low Temperatures* (MIT, Cambridge, Massachusetts, 1949), p. 108; Phys. Rev. **77**, 750 (1949).

[15] R. J. Higgins, J. A. Marcus, and D. H. Whitmore, Bull. Am. Phys. Soc. **7**, 231 (1962); **9**, 240 (1964).

[16] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 651.

[17] R. J. Higgins, J. A. Marcus, and D. H. Whitmore, Phys. Rev. **137**, A1172 (1965). Other experimental work on zinc is listed in Refs. 10–20 and 33 of this paper.

[18] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 439 (1962).

[19] Walter A. Harrison, Phys. Rev. **126**, 497 (1962).

[20] Walter A. Harrison, Phys. Rev. **118**, 1190 (1960).

[21] V. Heine, Proc. Phys. Soc. (London) **69**, 505 (1956).

[22] R. J. Higgins, thesis, Northwestern University, 1965 (unpublished; available on microfilm from University Microfilms, Ann Arbor, Michigan).

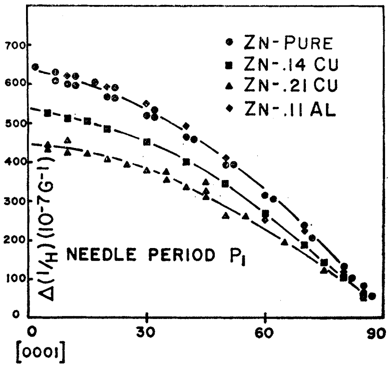

FIG. 2. Effect of alloying on the needle period P_1. Period (units of $10^{-7}\ G^{-1}$) is plotted as a function of the angle of the magnetic field away from the [0001] direction. (The results are identical in both the $(11\bar{2}0)$ and $(10\bar{1})$ planes.)

to be an electron segment. The problem is that the Heine model[21] and similar models[23] which calculate only the Fermi energy change are inadequate for noncubic metals like zinc, in which alloying produces changes not only in the electron concentration Z but also in the axial ratio c/a. The shape of the Brillouin zone changes, so that the relative size of various NFEFS segments can change even at constant Z and constant volume. This has been recognized by Harrison,[20] who showed that in the case of the needle period P_1, the parameter which expresses the amount of overlap producing P_1 is Za/c, so that axial ratio is as important as electron concentration. Harrison's approach will be used in accounting for the changes in the two longest periods in zinc. It will be seen that a specific geometrical formula must be worked out for each Fermi surface orbit, and that in no case can the sign of the observed change in period be simply related to the electron or hole character of the orbit.

EXPERIMENTAL PROCEDURE

Alloy single crystals were prepared from starting materials of 99.999% purity. Crystals were grown by the Bridgman technique in pyrex molds, starting with appropriate amounts of pure zinc and a chemically analyzed master alloy. Samples were cut with an acid saw from the center of long bar crystals to minimize concentration gradients. Some of the samples were chemically analyzed and found to be within 0.01% of the weighed composition. A plot of residual resistance ratio versus weighed chemical composition was linear.

Oscillatory torques in a magnetic field were measured with a torsion balance designed and built by J. H. Condon.[24] The success of these alloy experiments was essentially due to the high sensitivity ($<10^{-3}$ dyne cm) of this torsion balance. In fact, all but one of the dHvA oscillations observed in pure zinc[17] were detected in alloys containing up to 0.21% Cu (residual resistance ratio 80). Samples were x-ray oriented and mounted on quartz rods with axes within 1° of particular crystallographic directions. Care was taken with the orientation so that period changes on alloying were not in fact due to misorientation.

Samples were suspended from the torsion balance in a bath of liquid helium, whose temperature could be lowered to 1.19°K by pumping. Applied magnetic fields up to 33 kG were supplied by a conventional electromagnet. (Magnetic field directions will be specified relative to *real space* crystallographic directions.) dHvA oscillations were recorded continuously as a function of $1/H$[25] on an XY recorder. These and other experimental details are described elsewhere.[17,22]

EFFECT OF ALLOYING ON THE NEEDLE PERIOD P_1

Results

The angular dependence of period P_1 is shown in Fig. 2, and is identical in both the $(11\bar{2}0)$ and $(10\bar{1}0)$ planes. Three results are seen in Fig. 2. First, alloying with copper lowers the period, raising the area of the segment. Second, the shape of the needle remains relatively constant: an expansion of Fig. 2 90° from [0001] shows that period changes are of slightly smaller percentage than those at [0001], which amount to 30% for 0.21% Cu. Third, the addition of 0.11% Al raises the period slightly, but the points fall within the 4% uncertainty of pure zinc periods. An attempt was made to corroborate this conclusion by measuring periods in a Zn-0.17% Al alloy, but the amplitudes were so low as to cast doubt on the quality of the crystal.

Interpretation

In the NFEFS, the needle is formed by overlap of the free-electron sphere across the edge of the Brillouin zone near the point K (Fig. 3). The free-electron-sphere radius k_f extends less than 1% beyond the point K, so that a sizeable band gap would shrink the needle out of existence in pure zinc. There is thus some justification for using the NFEFS model (zero band gap) as a first-order model for explaining alloying changes in P_1. The smallness of overlap also indicates that large fractional changes in needle area can occur due to small changes in electron concentration and axial ratio. It is possible to estimate the dependence of cross-sectional area on these factors for $\mathbf{H}||[0001]$ by a geometrical approximation. Referring to Fig. 3, the distance l is given by

$$l = k_F - (1/\sqrt{3})b_1. \tag{4}$$

The area of the needle may be approximated by the area πl^2 of the inscribed circle (approximation I) of

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[23] V. Kosevich, Zh. Eksperim. i Teor. Fiz. 35, 249 (1958) [English transl.: Soviet Phys.—JETP 8, 229 (1959)].

[24] J. H. Condon and J. A. Marcus, Phys. Rev. 134, A446 (1964).

[25] R. J. Higgins, Rev. Sci. Instr. 36, 1536 (1965).

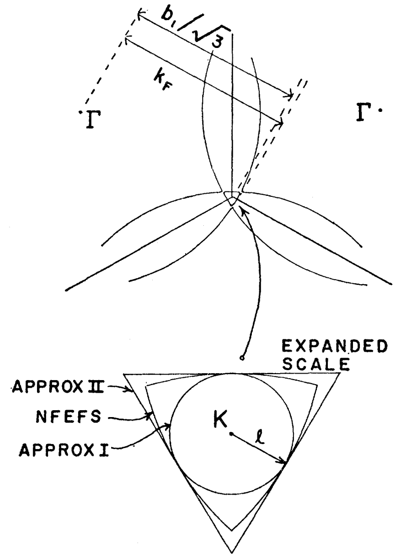

FIG. 3. Geometrical approximation of the NFEFS needle area for $H||[0001]$. Approx. I is that used in the text; Approx. II is presumably the one used by Harrison (Ref. 20). The important point is that either approximation is pinned to the actual NFEFS orbit at three points, hence will follow area changes as long as no shape change is involved (band gap effects).

radius l. Writing k_F in terms of electrons/atom Z and real space lattice parameters a and c, the approximate needle area is[26]:

$$A_I=\frac{4\pi}{9}\left(\frac{2\pi}{a}\right)^2\left[\left(\frac{27\sqrt{3}Z}{16\pi c/a}\right)^{1/3}-1\right]^2. \tag{5}$$

The extreme sensitivity of A_I to alloying follows from the near cancellation of the quantity in brackets in Eq. (5). With $Z=2.00$ and $c/a=1.830$,[27] that quantity is $[1.00563-1.00000]$. The fractional change in area for a fractional change in Z or c/a is given by

$$\frac{\partial \ln A}{\partial \ln Z}=-\frac{\partial \ln A}{\partial \ln(c/a)}=\frac{\frac{2}{3}(\beta Z/(c/a))^{1/3}}{[(\beta Z/(c/a))^{1/3}-1]}, \tag{6}$$

where $\beta=27\sqrt{3}/16\pi$, which in the limit of infinite dilution corresponds to a 130% increase in area with a 1% increase in Z and a corresponding *decrease* in area for a 1% increase in c/a. Axial ratio is therefore of equal importance as electron concentration in determining the size of this particular FS segment, and accounts for the observed dHvA period changes. Figure 4 (data from Pearson, Ref. 27) shows the effect of alloying on the axial ratio[28] and the parameter $Z/(c/a)$, which determines the overlap of the Fermi sphere [Eq. (5)]. It is seen that in Zn-Al alloys the Z and c/a changes cancel so that the over-all needle overlap does not change, in accord with the experimental observation of a negligible change in dHvA period. In Zn-Cu alloys, however, c/a decreases at a rate more than twice as fast as the rate at which Z decreases. The needle area should increase, as observed experimentally, in spite of the fact that the needle is an electron segment and alloying with Cu presumably takes away electrons. This demonstrates the importance of the *shape* of the Brillouin zone in the interpretation of FS changes in noncubic metals.

The model also accounts semiquantitatively for the magnitude of the observed area changes in Zn-Cu alloys, as shown by the square points in Fig. 5. (Ref. 28) calculated from Eq. (5). The model area [Eq. (5)] in pure zinc is nearly a factor of 2 larger than the observed area, due to the neglect of band-gap effects. Shrinkage of A_I in pure zinc would result in larger fractional changes on alloying, which is in the right direction to account for the discrepancy in Fig. 5 between theory (■) and experiment (●). This may be demonstrated by representing the band-gap effect as in incremental decrease Δk_F in k_F. Assuming that Δk_F is insensitive to alloying at these low concentrations, and choosing Δk_F to make A_I (pure Zn) equal to the observed area results in the (▲) points in Fig. 5.

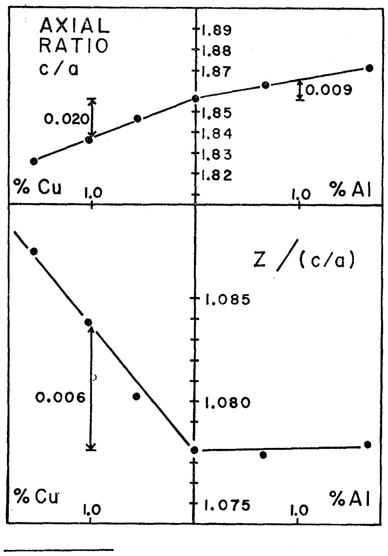

FIG. 4. Changes in the axial ratio c/a (room temperature) and the parameter $Z/(c/a)$ of zinc due to addition of Cu (left) or Al (right) impurities. Data taken from Pearson's Tables (Ref. 27).

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[26] This formula reproduces the result quoted by Harrison (Ref. 20) except for a constant factor. Our interpretation of alloying data which follows is an extension of the discussion by Harrison, except that our more accurate dHvA data and recent low-temperature lattice parameter measurements (Ref. 27) allow a more definite conclusion to be drawn.

[27] 4.2°K lattice parameters for pure zinc were obtained by combining room temperature lattice parameters from W. B. Pearson, *Lattice Spacings and the Structure of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), p. 886, with the differential thermal expansion data down to 4.2°K of R. W. Meyerhoff and J. F. Smith, J. Appl. Phys. **33**, 219 (1962). Reciprocal lattice vectors in the basal plane will be referred to as $\mathbf{b}_1$ and $\mathbf{b}_2$, and $\mathbf{b}_3$ perpendicular to the basal plane, and are related to lattice parameters $\mathbf{a}_i$ by the usual relations $\mathbf{a}_i\cdot\mathbf{b}_j=2\pi\delta_{ij}$.

[28] In the absence of low-temperature alloy lattice parameter measurements, the assumption has been made that the percentage thermal contraction from room temperature to 4.2°K is the same for the dilute alloys as for pure zinc, so that the *percentage* change on alloying of the room temperature lattice parameters (Pearson, Ref. 27) may be used at 4.2°K, with absolute value determined by the known value for pure Zn at 4.2°K (Ref. 27).

Search for Change in the Needle Effective Mass on Alloying

The cyclotron effective mass [Eq. (2)] of an electron orbit may be obtained from the temperature dependence of the dHvA torque amplitudes[29,30]:

$$H^{3/2}\left(\frac{\pi^2kTm^*}{\mu_BHm_0}\right)\left[\sinh\left(\frac{\pi^2kTm^*}{\mu_BHm_0}\right)\right]^{-1} \times\exp\left(-\frac{\pi^2kXm^*}{\mu_BHm_0}\right), \quad (7)$$

where X is the scattering "temperature"[30] and μ_B is the Bohr Magneton.

In view of the large period changes in Zn-Cu alloys, it was of interest to look for mass changes as the Fermi energy is shifted, since anomalies in the energy spectrum will appear first in the mass ($\propto \partial A/\partial E$). The effective mass of a NFEFS orbit is proportional to its circumference, or roughly proportional to the square root of the area.[31] A NFEFS mass will therefore change roughly half as fast as the area (Fig. 5), reaching about 14% with 0.21% Cu. A mass change much larger than this has been observed in zinc under hydrostatic pressure.[32]

There are two problems in accurate mass calculation, both associated with the smallness of the needle mass ($m^*/m_0=0.0075$ for $H\|[0001]$). First, the hyperbolic-sine term in Eq. (7) may not be replaced by an exponential, so that calculation of the mass from the ratio of amplitudes at two temperatures must be done iteratively.[22,33] Second, the small mass makes the amplitude factor $x/(\sinh x)$ relatively temperature insensitive. A small error in reading an amplitude (e.g., 2%) makes a large error in the mass (20% for $m^*/m_0=0.01$, $T=2°\text{K}$, $H=5\times10^3\text{G}$). This error was minimized by going to higher temperatures and lower fields, although this procedure resulted in experimental difficulties in measuring smaller amplitudes.

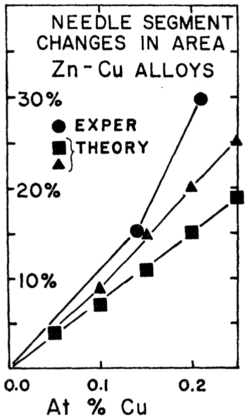

FIG. 5. Percentage area change of the needle as a function of copper content for $H\|[0001]$. Calculated points ■ correspond to NFEFS areas [Eq. (5)] and ▲ to a modified NFEFS in which the Fermi radius for pure zinc has been shrunk down to agree with the observed dHvA area.

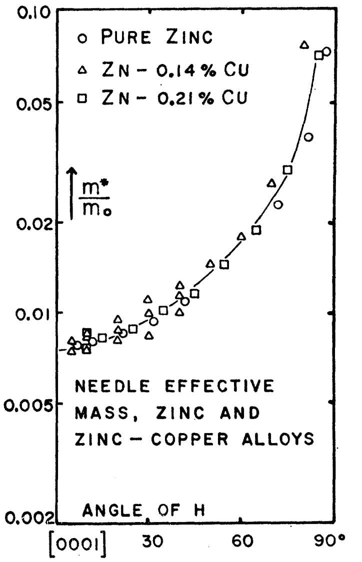

FIG. 6. Needle effective mass in zinc and Zn-Cu alloys, plotted on a logarithmic scale. The masses are identical in both the $(11\bar{2}0)$ and $(10\bar{1}0)$ planes. Where there are several points at a single angle, the mass was evaluated with more than one temperature pair.

The calculated needle effective mass values are shown in Fig. 6. The values for pure zinc agree with those of Joseph and Gordon.[18] There appears to be no systematic alloying effect on m^* for up to 0.21% Cu, within the estimated ±10% uncertainty in the results. Alloying effects are therefore not larger than what the NFEFS model predicts.

EFFECT OF ALLOYING ON THE SECOND LONGEST PERIOD P_2

Results

This dHvA oscillation has been assigned by Harrison[19,20] to an orbit on the multiply connected second-band hole segment of the NFEFS; the orbit is referred to as the horizontal arm. Our results[22] for P_2 as a function of magnet angle agree with those of Joseph and Gordon[18] to within 2% for period and 5% for effective mass, and will therefore not be discussed in detail. We have, however, been able to track this period to angles further from $[11\bar{2}0]$ by the use of rotation curves (oscilations at fixed field as a function of magnet angle), and have observed the amplitude to disappear within

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

[30] R. B. Dingle, Proc. Roy. Soc. **A211**, 517 (1952).

[31] This qualitative conclusion is confirmed by a calculation using the approximate area A_I of Eq. (5) (see Ref. 22, p. 121).

[32] I. M. Dmitrenko, B. I. Verkin, and B. G. Lazarev, Zh. Eksperim. i Teor. Fiz. **35**, 328 (1958) [English transl.: Soviet Physics—JETP **8**, 229 (1959)]. A pressure which lowered the cross-sectional area of the needle by 26% *raised* the mass by almost a factor of 2. This mass change seems anomalously high and is opposite in sign from what the NFEFS predicts.

Note added in proof. This mass change under pressure has not been observed in more recent measurements [W. O'Sullivan, (private communication)].

[33] R. J. Higgins, J. A. Marcus, and D. H. Whitmore, *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum Press, Inc., New York, 1965).

half a degree when H is 68° from the [$11\bar{2}0$] directions of maximum period. This suggests either the disappearance of an extremal area orbit or (through the spin-splitting term in the dHvA amplitude[29]) of an effective mass ratio of 0.5. The latter suggestion is partially supported by our measurement[22] of an effective mass which passes through 0.3 at 60° and *extrapolates* to 0.5 at H 70° from [$11\bar{2}0$].

Alloying results are shown in Fig. 7.[34] Changes in period of opposite sign are observed with these monovalent and trivalent solutes, copper decreasing and aluminum increasing the period (in sharp contrast to the P_1 results, where an equal concentration of Al left P_1 essentially unchanged). The period at [$11\bar{2}0$] is plotted in Fig. 8 as a function of composition. The slope of the straight line drawn through the pure Zn and Zn-Cu points is equivalent to a 14% decrease in period for only 0.1 at.% Cu. An extension of this line onto the Zn-Al side suggests that the effect of Al is somewhat smaller, roughly a 7% increase in period per 0.1% Al.

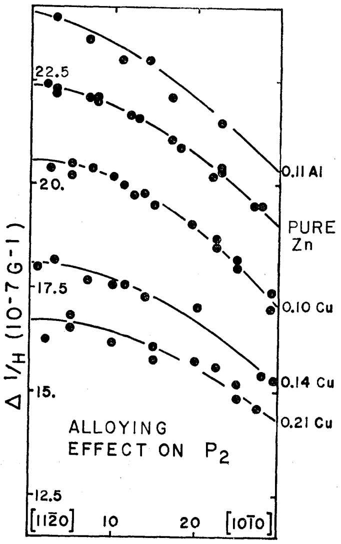

Fig. 7. Effect of alloying on the period P_2, over 30° range of field directions.

Interpretation

The predominant feature of alloying changes in the period P_2 is the large magnitude, comparable to P_1 changes in spite of the fact that P_2 corresponds to an extremal area 30 times larger than P_1.[35] The opposite sign of the changes with Cu and Al is also of interest since it lends credence to the simple picture that alloying simply subtracts or adds electrons to the NFEFS. Interpretation of these results is complicated by the fact that the observed area in pure zinc is a factor of 10 smaller than the NFEFS value, a larger modification of the NFEFS than is required to assign any of the other periods. The lattice potential therefore has a large effect on the size of this orbit in pure zinc,[19] and it may be expected that band-gap effects will complicate the interpretation of alloying effects.

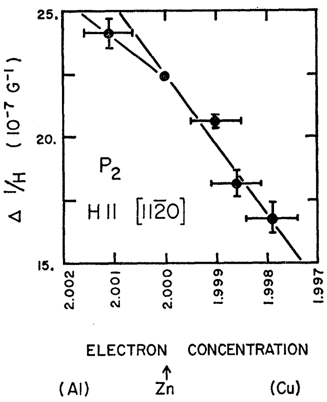

Fig. 8. Composition dependence of P_2 for $H\|[11\bar{2}0]$. The total uncertainty in chemical composition is estimated to be 0.01 at.%. The uncertainty in period becomes larger with alloying due to the smaller amplitude. The line drawn through points on the Zn-Cu side has been extended to the Zn-Al side to show that Zn-Al alloying changes appear to be smaller than Zn-Cu alloying changes.

An approximate geometrical calculation of the area of the horizontal arm orbit for $H\|[11\bar{2}0]$ has been performed, similar to the calculation of needle orbit areas, in order to determine whether electron concentration and axial ratio changes alone provide an adequate explanation for the *sign* of the observed changes in P_2. Since the size of the NFEFS area of this orbit does not agree well with experiment in pure zinc, it was not expected to account for the *magnitude* of the alloying

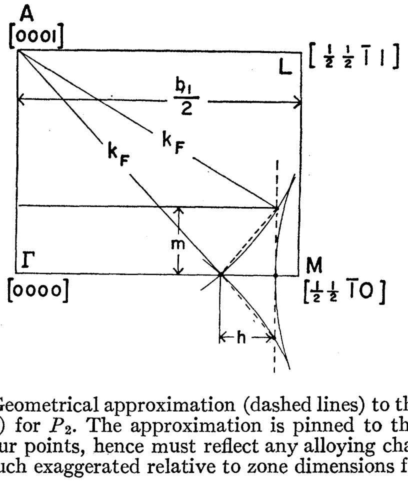

Fig. 9. Geometrical approximation (dashed lines) to the NFEFS (solid arcs) for P_2. The approximation is pinned to the NFEFS orbit at four points, hence must reflect any alloying changes. Size of orbit much exaggerated relative to zone dimensions for clarity.

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[34] In any 30° region there are actually 3 branches of P_3 since the dHvA oscillation from any individual horizontal arm can be tracked for more than 60° monotonically decreasing in period. Only the top branch is shown in Fig. 7 since the amplitude of the lower branch oscillations was very small in the alloys.

[35] If alloying adds electrons in uniform density over the FS (as is the case in the NFEFS model) then *fractional* change in period should go as the circumference over the area, or roughly as $P^{1/2}$. On the basis of this simple picture, fractional changes in P_2 should be a factor of 5 less than changes in P_1. A different approach using measured effective masses (as in Ref. 21) but still neglecting axial ratio changes predicts that P_2 will change *half* as fast as P_1.

results. The approximate area (Fig. 9) is $(m)(h)$, where

$$m=b_3-k_F[1-((b_1/k_F)-1)^2]^{1/2} \qquad (8)$$

and

$$h=b_1-k_F\{1+[1-(b_3/k_F)^2]^{1/2}\}\,. \qquad (9)$$

In pure zinc, the approximate area is within 10% of the NFEFS area evaluated graphically.

Substitution into Eqs. (8) and (9) of alloy lattice parameters[28] and free electron sphere radius appropriate to 0.1% Cu or Al gives area changes of the observed sign in both cases, *but of only 1% magnitude* rather than 14% (0.1% Cu) or 7% (0.1% Al). The NFEFS area in pure zinc can be brought into agreement with the observed area by raising k_F by 3.5% (effectively turning on the lattice potential). It is of interest to check whether this shrunken NFEFS segment adequately represents alloying changes. Substitution of alloy lattice parameters and free electron sphere radius for 0.1% Cu or Al now gives area changes of 3%, still much smaller than the observed changes.

EFFECT OF ALLOYING ON THE THIRD LONGEST PERIOD P_3

P_3 is a factor of 10 shorter than P_2 and a factor of 300 shorter than P_1. On the basis of the NFEFS a change of less than 1% for 0.1% Cu would be expected. However, if P_3 is as anomalous in its alloying behavior as P_2 is, a change of about 5% would occur. Measurements of the several branches of P_3 in a 0.21% Cu alloy show periods essentially identical with those of pure zinc (Fig. 10). There are no alloying changes greater than the scatter of ±1%.

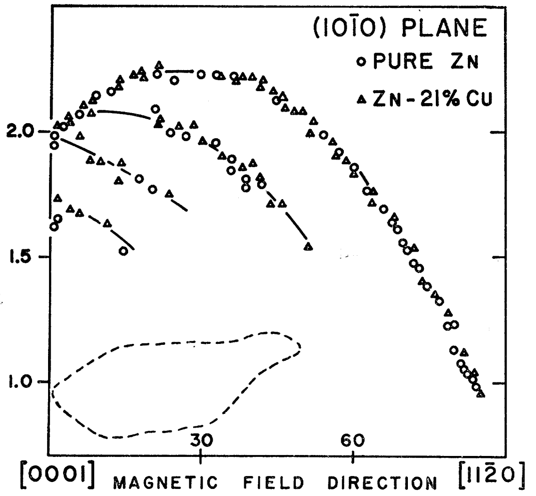

FIG. 10. P_3 in the (10$\bar{1}$0) plane. Circles: pure zinc. Triangles: Zn-0.21% Cu. There appears to be no systematic change in the curves of P_3 due to alloying. The dashed curve defines a region of shorter periods which though they could not be determined accurately, do not appear to change with alloying.

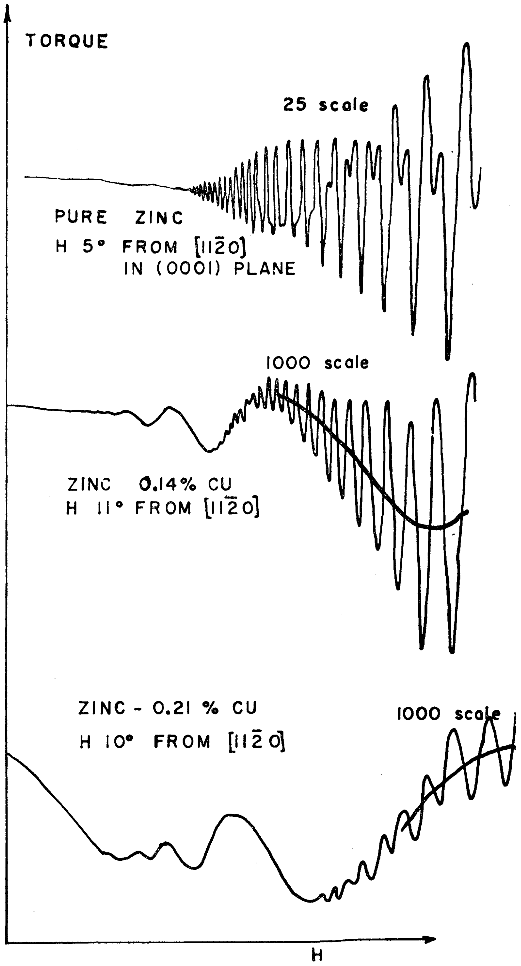

FIG. 11. Alloy period P_A in two Zn-Cu alloys in the (0001) plane compared with a field sweep in pure Zn at a similar orientation. Torque is plotted as a function of magnet current, the low-field end being on the left (the oscillations are therefore not periodic across the page). The alloy period is seen at low fields before being obscured by the shorter period P_2. The zero crossings of P_2 have been drawn in to show how P_A causes a baseline shift at high fields. The structure in the top curve is caused by a near second harmonic to P_2, and should not be confused with a low-frequency oscillation.

The branches of P_3 come together at [0001], giving long beats near [0001]. Besides these long beats, shorter beats (P_4 and P_5) occur which indicate two hidden periods about 20% shorter than P_3 at [0001]. P_4 and P_5 have been interpreted[18] as orbits on the monster arm junction and cap at the point H, which have been split by spin orbit coupling. In the Zn-Cu alloys, it was observed that the beat structure of P_4 is unchanged from that of pure Zn; no change in the spin orbit energy gap was detected. This is consistent with the fact that spin orbit coupling increases gradually with atomic number.[36]

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[36] We are indebted to L. Liu for a helpful discussion on spin-orbit coupling.

P_A: A LONG PERIOD OBSERVED IN ZN-CU ALLOYS

In the course of measurement of P_2 in alloys with fields in the (0001) plane, traces were seen at lower fields of a period 20 times longer than P_2, which will be designated P_A, the alloy period (Fig. 11). Only three or four cycles could be observed, because the amplitude became unmeasurably small at the low field end and became obscured by the larger amplitude of P_2 at the high field end. This long period does not appear to be present in pure Zn (Fig. 11, top). In spite of the difficulty of accurate period determination with so few cycles of oscillation, certain qualitative conclusions can be drawn concerning the orientation and composition dependence of P_A (Fig. 12). The period has a maximum for $H||[11\bar{2}0]$, so that the corresponding Fermi surface section has a minimum cross-sectional area at this angle, which increases as H is turned away from $[11\bar{2}0]$. It was not possible to determine the orientation dependence of P_A for fields out of the (0001) plane because P_A then becomes obscured by the large amplitude of P_1.[37] P_A appears to decrease with increasing copper content (Fig. 12), falling from about 460×10^{-7} G^{-1} (0.14% Cu) to about 400×10^{-7} G^{-1} (0.21% Cu) for $H||[11\bar{2}0]$. No trace of P_A was seen in a 0.10% Cu crystal, or in a 0.11% Al crystal.

Since P_A has a value quite close to the value which P_1 has for $H||$ to [0001], a bicrystal could possibly contribute a spurious oscillation due to P_1. This possibility has been effectively eliminated by verifying that P_A has hexagonal symmetry. We are unable to place this segment on the NFEFS model. The problem is that essentially all of the smaller extremal areas of the NFEFS have been observed in pure zinc,[17,18] leaving virtually no place to assign a new oscillation. However, published evidence for the 4th-band cigars is limited, consisting of observations for fields only near [0001] and no observations for fields in the (0001) plane.[17] But the cross-sectional area of the 4th-band cigar for H along $[11\bar{2}0]$ corresponds to a period of 3.7×10^{-7}, a factor of 100 smaller than the observed period P_A. A more likely region for the appearance of a new extremal area is the region of the needle, near the symmetry point K, where the Fermi surface nearly pulls away from the zone edge. It has been found in the case of magnesium[38] that the band structure is complex in this region. There is a point of contact (without spin-orbit coupling) between the needle and the second-band hole segment, the position of which is very sensitive to the value of the Fermi energy (and presumably the axial ratio as well). It would be of interest to examine this region in the band structure of zinc, to see if, as has been suggested,[39] similar contact between bands occurs which could explain the appearance of P_A.

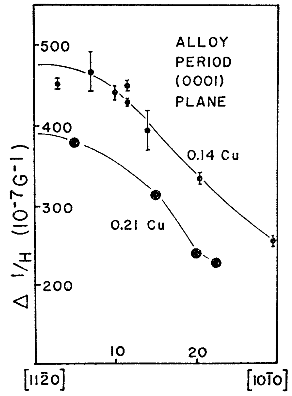

FIG. 12. Alloy period in Zn-0.14% Cu and Zn-0.21% Cu. The error bars on the 0.14% Cu periods are the computer-calculated standard deviation σ from a least-squares fit:

$$\sigma=\left[\Sigma_1{}^N\,(1/H_{\mathrm{exp}}-1/H_{\mathrm{calc}})^2/(N-1)\right]^{1/2}.$$

OBSERVATION OF HIGHER FREQUENCY OSCILLATION IN ALLOYS

Besides the long periods already described, a search was made for the high-frequency oscillations[17] in a crystal containing 0.21% Cu with fields in the $(10\bar{1}0)$ plane. All of the high-frequency oscillations of pure zinc were detectable, though of reduced amplitude. F_9 and F_6 (notation of Ref. 17) were easily resolvable, and gave values of frequency identical to those in pure zinc. The spectrum of high frequencies was not investigated in detail in the alloys, since these larger pieces of the Fermi surface have small fractional changes in size due to alloying. However, the observation in dilute alloys of all of the known Fermi-surface pieces indicates that the de Haas–van Alphen effect is well suited to dilute alloy studies.

CONCLUSIONS

1. The nearly-free electron constructions employed in the body of this paper should be viewed as a simple attempt to interpret what is certainly a complicated phenomenon: the effect of alloying on the size of various sections of the zinc FS. The main success of the model is in demonstrating that the axial ratio c/a is as important as the electron concentration Z. For the needle orbit (P_1), the combination of these factors makes it possible, as pointed out earlier,[20] for Cu ($Z=1$) to *increase* the size of an electron orbit, rather than decrease it as would be expected from the lowering of Z. The balance between Z and c/a in the case of Al ($Z=3$) impurities explains the *negligible* change in the needle area in a Zn-Al alloy. The relation between Z and c/a is more complicated for the horizontal arm orbit (P_2) but a straightforward application of the NFE model gives the observed sign of the alloying changes in both Zn-Cu and Zn-Al.

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[37] The torque amplitude of P_1 is zero for fields in the (0001) plane because the extremal area is constant in this plane (Ref. 29, footnote to p. 640). In fact P_A is easily obscured by P_1 if the crystal is misoriented by a few degrees.

[38] M. G. Priestley, L. M. Falicov, and Gideon Weisz, Phys. Rev. **131**, 617 (1963).

[39] R. W. Stark, Phys. Rev. **135**, A1698 (1964).

2. The zero-band-gap model underestimates the change in needle area by a factor of two. Turning on the lattice band gap in a phenomenological way by shrinking the needle area to agree with the dHvA area in *pure* zinc increases the sensitivity to alloying, but still not enough to agree with the alloying data. Any interpretation of this discrepancy must be made with caution in view of the extreme sensitivity of the needle area to the lattice parameters which are only approximately known.[28] The direction of the discrepancy is such as to be accounted for by a lower lattice potential in Zn-Cu than in pure Zn, which is at first puzzling in view of the very strong lattice potential in pure Cu.[40] However, the band structure in the region of the needle is complicated by the suggestion[39] that there is an accidental degeneracy (split by spin-orbit coupling) like that which has been calculated for magnesium.[38] Motion of the point of degeneracy *toward* the central extremal area would increase the extremal area in accord with the dHvA results. In magnesium, the degeneracy shifts towards the center of the needle as the Fermi energy is *raised*.[38] We note that in zinc, the volume per atom decreases[20] on adding Cu at a rate fast enough to offset the Fermi radius decrease, so that the *free electron* Fermi energy *increases* very slightly ($dk_F/k_F \cong +0.00008c$, c in % Cu).

3. The model *underestimates* the magnitude of the increase in the area of P_2 due to Cu by a factor of 10 (zero band gap) or by a factor of 3 (k_F raised by 3.5% to shrink the pure zinc area to agree with the dHvA area; a phenomenological band gap correction). It is unlikely that a discrepancy of this size is due to uncertainty in lattice parameters. The direction of the discrepancy suggests a lowering of the lattice potential due to Cu impurities. Such a mechanism will be outlined briefly in the hope of inspiring an explicit calculation. The crucial point is that not all of the lattice band gaps are negative in sign.[19] In pseudopotential language, the orthogonalized-plane-wave form factor versus wave number calculated by Harrison[41] passes through zero such that $V(002)<V(100)<0<V(101)$ where $V(q)=\langle k_F+q|W(k_F)|k_F\rangle$,[41] and the notation for the reciprocal lattice vectors is that of Harrison[19]). Any perturbation which acts to shift $V(q)$ uniformly downward will *decrease* the magnitude of $V(101)$ while increasing the magnitude of $V(002)$ and $V(100)$. Since two of the three corners of the P_2 orbit correspond to (101) Bragg reflection, such a perturbation will tend to *increase* the area of the orbit. It is of interest to note that a linear combination of the $V(q)$ for zinc with that calculated for copper[42] provides such a perturbation.

4. An unexplained result is the observation of a period of order $400\times10^{-7}\ G^{-1}$ for fields in the (0001) plane in crystals containing 0.14 and 0.21% Cu, but not with 0.10% Cu, pure Zn, or 0.11% Al. Only three or four cycles could be observed because of the dominance of other periods, so that accurate orientation dependence could not be obtained.

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[40] B. Seegal, Phys. Rev. **125**, 109 (1962).

[41] Walter A. Harrison, Phys. Rev. **129**, 2512 (1963).

[42] Walter A. Harrison, Phys. Rev. **131**, 2433 (1963). Note that Harrison emphasizes that the form factor for copper is of dubious validity.