Magnetic Breakdown in Zinc and Its Alloys as Seen in the de Haas–van Alphen Effect*

R. J. HIGGINS†
Materials Science Department, Northwestern University, Evanston, Illinois
and
Department of Physics, University of Oregon, Eugene, Oregon

AND

J. A. MARCUS
Department of Physics, Northwestern University, Evanston, Illinois

(Received 24 April 1967)

The amplitude of the longest-period de Haas–van Alphen oscillation in zinc has been measured as a function of magnetic field strength and field direction in pure zinc and dilute alloys. The field dependence, which is anomalous at high fields, was fitted by the Lifshitz-Kosevich (LK) expression modified to include magnetic breakdown, using a correction factor due to Pippard. This expression fits the data well for field directions up to 70° from [0001], and gives accurate values of the breakdown field parameter H_0. Values of H_0 obtained for pure zinc by this method range from 2.2 kG (**H**‖[0001]) to 10 kG (**H** 70° from [0001]), with fields in either the $(10\bar{1}0)$ or $(11\bar{2}0)$ plane. These results are interpreted as evidence that the lattice band gap is essentially constant over the central third of the needle, the angular dependence of H_0 being due to the velocity term in Blount's expression for H_0. Values of the Dingle scattering temperature ($X=1.5$°K in this sample) show no angular dependence; the scattering relaxation time is therefore isotropic on the needle. This result disagrees with previous measurements, but the conflict is shown to be due to the persistence of magnetic breakdown to very low fields, which invalidates the usual graphical procedure for evaluating X. In amplitude measurements on *impure* systems (0.14% Cu, 0.21% Cu, 0.11% Al, 0.008% Mn), magnetic breakdown is far less apparent than in pure Zn. High values of H_0 (>5 kG) result from a fit to the breakdown-corrected LK expression. Arguments about band-gap changes are unable to explain this result satisfactorily. The increase in H_0 correlates with the decrease in the measured scattering relaxation time. It is suggested that the Pippard breakdown correction, based on a coupled phase-coherent network of orbits, is not appropriate in the presence of strong impurity scattering. An alternative breakdown correction is derived, appropriate to the random-scattering limit, using a generalization of the Dingle scattering factor due to Brailsford and a breakdown-scattering probability suggested by Condon. It is shown that this results in a high-field amplitude qualitatively similar to that observed in the alloys, without changing the value of H_0 (obtained from pure zinc where the Pippard approach is valid). Further measurements and theoretical calculations are suggested.

INTRODUCTION

THE de Haas–van Alphen (dHvA) oscillations in magnetic susceptibility are a well-understood phenomenon in the sense that there exists a theoretical expression developed by Lifshitz and Kosevich (LK)[1] which adequately describes the period, termperature dependence, and magnetic field dependence. Anomalous deviations from this expression exist in several metals. In zinc, for instance, the amplitude at high fields of the longest period (needle) oscillation[2] is much smaller than the LK formula predicts, reaching a factor of 5 reduction at 10 kG. This phenomenon has been observed by several investigators,[3–6] with various attempts to fit empirical correction factors.

It is now thought that the explanation for the anomalous field dependence is magnetic breakdown,[7,8] the tunneling of electrons out of their orbits which can occur at high magnetic fields at locations in the orbit in k space where two bands are separated by a small band gap. In zinc, electrons on the needle can tunnel to the "monster" at three points on the orbit,[9,10] because of the

* Work supported by the National Science Foundation and by the Advanced Research Projects Agency through the Northwestern University Materials Research Center.

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

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

[2] For work on the dHvA spectrum of zinc and the experimentally derived Fermi surface, the reader is referred to Ref. 20 (low fields); R. J. Higgins, J. A. Marcus, and D. H. Whitmore [Phys. Rev. **137**, A1172 (1965)] (intermediate fields); A. C. Thorsen, L. E. Valby, and A. S. Joseph [*Low Temperature Physics*—LT9 (Plenum Press, New York, 1965), Part B, p. 867], J. G. Anderson and W. F. Love [Bull. Am. Phys. Soc. **10**, 349 (1965)], and M. G. Priestley and M. A. Mondino [*ibid.* **9**, 551 (1964)] (high fields); Ref. 23 (alloying effects); and W. J. O'Sullivan and J. E. Schirber [Phys. Rev. **151**, 484 (1966)] (pressure effects). For the purpose of this paper, it is sufficient to describe the needle segment of the Fermi surface: a long thin ellipsoid along the hexagonal axis, with major axis more than ten times the length of the minor axis, containing about 10^{-6} electrons per atom. The dHvA period is about 6.3×10^{-5} G^{-1} for H along the hexagonal axis, so that all but the last cycle of oscillation occurs below 15 kG.

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

[4] B. I. Verkin and I. M. Dmitrenho, Isvest. Akad. Nauk. SSSR **19**, 409 (1955) [English transl.: Bull. Acad. Sci. USSR **19**, 365 (1955)].

[5] T. G. Berlincourt and M. C. Steele, Phys. Rev. **95**, 1421 (1954).

[6] F. J. Donahue and F. C. Nix, Phys. Rev. **95**, 1395 (1954).

[7] Morrell H. Cohen and L. M. Falicov, Phys. Rev. Letters **7**, 231 (1961).

[8] E. I. Blount, Phys. Rev. **126**, 1636 (1962).

[9] A. B. Pippard, Proc. Roy. Soc. (London) **A270**, 1 (1962).

[10] A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A256**, 317 (1964).

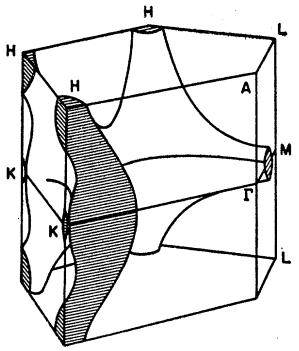

FIG. 1. A portion of the Fermi surface of zinc, showing the topology of the second-band "monster" relative to the third-band "needle." The needle, located at symmetry points K, has been exaggerated in size for clarity.

smallness of the band gap (0.02 eV) at these points. The relevant topology is shown in Fig. 1. Tunneling acts as a scattering mechanism which produces marked changes in the magnetoresistance[11,12] at fields above 2.5 kG in zinc, the same field region where the dHvA amplitude anomaly becomes appreciable. Physically, as fewer electrons complete their orbits around the needle, the dHvA oscillation becomes smaller. To define this correlation more precisely requires a quantitative comparison between the dHvA amplitude data and a calculation of dHvA amplitudes including breakdown. It is the aim of Sec. I of this paper to provide such a comparison, including a test of several theoretical models.[10,13–15] Such a test has been attempted,[16] but was restricted for experimental reasons to fields below about 2 kG. This restriction introduces some ambiguity, since several models can fit the functional dependence over a limited field range. In the present measurements, which have been reported in preliminary form earlier,[17] a field range of 1 to 30 kG was used, providing a stringent test of the theory over a wide range of breakdown probability. A similar fit to the dHvA amplitude with magnetic breakdown has been performed recently for magnesium,[18] with H along [0001]. The present results for zinc are complementary, but, in addition, provide breakdown information over a far wider region of magnetic field directions. The data are the first to be fit using a least-squares method, resulting in "best-fit" values of breakdown field with high accuracy for a given model. Least-squares values of the Dingle[19] scattering "temperature" X are obtained simultaneously, and show no dependence on field direction, in disagreement with previous measurements.[20] An explanation for the disagreement is found in the persistence of magnetic breakdown effects to fields below 1 kG, invalidating the usual graphical procedure for calculating X.

It is readily apparent from an inspection of raw data that the high-field dHvA amplitude of the needle oscillation in *dilute alloys* does not display the anomalous decrease observed in pure zinc and attributed to magnetic breakdown. It is known experimentally[12] and theoretically[21] that the apparent magnetic breakdown field observed in the *magnetoresistance* moves to higher fields with decreasing relaxation time (increasing impurity). However, this is not expected in equilibrium properties, such as the dHvA effect, according to a recent calculation.[14] Complications in both the experimental observations and theoretical interpretation prevent a quantitative interpretation of the dHvA observations. However, in Sec. II, the gross feature that magnetic breakdown becomes less likely in dilute alloys will be shown to be in apparent conflict with existing theory, and an alternative explanation involving impurity scattering will be developed.

EXPERIMENTAL

The dHvA measurements were made at temperatures ranging from 1.2 to 4.2°K in magnetic fields of 1 to 30 kG, using a Condon[22] torsion balance. The crystals were x-ray oriented and mounted with the torsion axis along $[10\bar{1}0]$ or $[11\bar{2}0]$ directions. The pure zinc crystals were kindly supplied by W. A. Reed of the Bell Telephone Laboratories. The alloy crystals were grown by the Bridgeman technique as described earlier.[23] Torque oscillations were recorded on the y axis of an x-y recorder, with inverse magnetic field $1/H$ plotted[24] on the x axis, spacing the oscillations equally across a page. The field sensor was a Hall probe calibrated by NMR.

The envelope of the dHvA oscillations was arrived at by drawing a smooth curve through the oscillation maxima, likewise for the minima; the amplitude of the envelope was measured every half-cycle of dHvA oscillation.

THEORY

The problem of including a correction for magnetic breakdown in the expression for the field dependence of the dHvA amplitude will be considered in this section. In a nearly-free-electron metal such as zinc, an electron orbit in a magnetic field is very nearly a series of arc segments, the corners of the orbit corresponding to wave vectors appropriate to Bragg reflection. Magnetic breakdown occurs when an electron continues on an arc segment rather than turning a corner. There is general agreement[8–10,25] that the probability P of magnetic

[11] W. A. Reed and G. F. Brennert, Phys. Rev. **130**, 565 (1963).
[12] R. W. Stark, Phys. Rev. **136**, A1698 (1964).
[13] W. A. Harrison, Phys. Rev. **126**, 1107 (1962); **129**, 2512 (1963).
[14] L. M. Falicov and Henryk Stachowiak, Phys. Rev. **147**, 505 (1966).
[15] R. G. Chambers, Proc. Phys. Soc. (London) **88**, 701 (1966).
[16] J. R. Lawson and W. L. Gordon, *Low Temperature Physics*—LT9 (Plenum Press, New York, 1965), Part B, p. 854.
[17] R. J. Higgins, J. A. Marcus, and D. H. Whitmore, *Low Temperature Physics*—LT9 (Plenum Press, New York, 1965), Part B, p. 859.
[18] R. W. Stark and L. M. Falicov (to be published).
[19] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 517 (1952).
[20] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 489 (1962).
[21] L. M. Falicov and Paul R. Sievert, Phys. Rev. **138**, A88 (1965).
[22] J. H. Condon and J. A. Marcus, Phys. Rev. **134**, A446 (1964).
[23] R. J. Higgins and J. A. Marcus, Phys. Rev. **141**, 553 (1966).
[24] R. J. Higgins, Rev. Sci. Instr. **36**, 1536 (1965).
[25] J. R. Reitz, J. Phys. Chem. Solids **25**, 53 (1964).

breakdown at any corner of the orbit is equal to

$$P=\exp[-H_0/H], \tag{1}$$

with the breakdown field H_0 given by[8]

$$H_0=\pi V_G^2/(4\hbar e|v_x v_y|). \tag{2}$$

G is the Bragg reflection wave vector, V_G is the energy gap between adjacent bands, H is taken to be parallel to the Brillouin zone face defined by G and defines the z direction, and v_x and v_y are normal and tangential components of the *free-electron* velocity evaluated at the zone face. When H is tilted away from the zone face, the velocity terms in Eq. (2) are expected to give an angular dependence to H_0 which corresponds to magnetic breakdown becoming less likely when an electron does not hit the Bragg reflection plane "head on."

In the absence of magnetic breakdown, the Lifshitz-Kosevich expression for the oscillatory free energy may be written[1,19,26,27]

$$F_{\rm osc}=KH^{5/2}\sum_{r=1}^{\infty}\frac{\Psi(r\gamma)}{r^{5/2}}\cos\left[\frac{rS_m}{\alpha H}-\phi_r\right]\times\cos\left[\frac{r\pi gm^*}{2m_0}\right]\exp\left[\frac{-\pi r}{\omega_c\tau}\right]. \tag{3}$$

Here, K involves numerical constants and the geometrical shape of the Fermi surface, $\Psi(x)=x/\sinh x$, $\gamma=(\pi^2kTm^*)/(m_0\mu_BH)$, m^* is the electron effective mass, μ_B is the Bohr magneton, r is the harmonic index, S_m is the Fermi-surface (FS) extremal area in momentum space, $\alpha=e\hbar/c$, g is the spin splitting factor (2 for free electrons), ω_c is the cyclotron frequency eH/m^*c, and τ is the Bloch-state lifetime in the presence of scattering. This last term is often rewritten to make the scattering factor resemble the temperature factor $\Psi(r\gamma)$ by defining the Dingle scattering "temperature"[19] X such that

$$\pi^2kXm^*/m_0\mu_BH\equiv\pi(\omega_c\tau)^{-1}. \tag{4}$$

In incorporating a correction for magnetic breakdown, it is helpful to note the origin of the exponential scattering factor in Eq. (3). In the absence of scattering, the density of electron states $n(E,k_z,H)$ at fixed k_z is a periodic series of delta functions of energy spacing $\hbar\omega_c$ (neglecting spin splitting). Evaluation of $F_{\rm osc}$ involves Fourier expanding n, with the Fourier expansion of the series of delta functions resulting in the series of cosine terms in Eq. (3). Scattering is introduced[19] by convoluting the delta function series with a Lorentzian line broadening $(\omega_c\tau/\pi)[1+(\omega_c\tau y)^2]^{-1}$, where $y=E/\hbar\omega_c$. The expression for $F_{\rm osc}$ [Eq. (3)] therefore includes exponential scattering factors, which are the Fourier components of the Lorentzian line broadening expanded in the energy interval $\hbar\omega_c$.

[26] M. H. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960).
[27] A. D. Brailsford, Phys. Rev. **149**, 456 (1966).

Following Chambers,[15] magnetic breakdown is incorporated into $F_{\rm osc}$ by writing an expression for $n(E,k_z,H)$ in the presence of magnetic breakdown and Fourier expanding; the rth Fourier coefficient B_r becomes the breakdown correction factor for the rth harmonic in $F_{\rm osc}$. This has been done analytically by Pippard[10] and clarified by Chambers,[15] using a *model* which bears some resemblance to the zinc problem: a three-sided orbit coupled to large circular orbits at each corner. In this case,

$$B_r=|q|^{3r}=[1-\exp(-H_0/H)]^{3r/2}, \tag{5}$$

where q is related to Eq. (1) by[9]

$$|q|^1=1-|p|^2,\quad \phi_p-\phi_q=\pm\tfrac{1}{2}\pi, \tag{6}$$

and p, the complex breakdown probability amplitude, is related to the breakdown probability P by

$$|p|^2=P. \tag{7}$$

A breakdown factor of *approximately* the form of (5) was also found by Pippard[10] for the complete coupled orbit network appropriate to zinc and magnesium.

An identical form has been obtained for B_r by Falicov and Stachowiak,[14] using an approximate Green's-function calculation of $F_{\rm osc}$ which is applicable to more complex coupled orbits as well.

Prior to the development of the coupled network models, Harrison[13] suggested a breakdown correction of the form

$$B_1(H)=Q^3=[1-\exp(-H_0/H)]^3, \tag{8}$$

where $Q=1-P$.

In interpreting the alloying results of Sec. II, the assumption will be made that the dHvA amplitude contains a *product* of two *separate* correction factors, one for scattering [the Dingle factor in Eq. (3)] and one for magnetic breakdown [the Pippard formula, Eq. (5)]. This product form is equivalent to the assumption that the Landau levels are broadened by two *independent* mechanisms: impurity scattering and magnetic breakdown, and is implicit in the treatment of Falicov and Stachowiak.[14] The product form is independent of the details of the broadened line shape, as follows from the convolution theorem. The Landau level is convoluted both by breakdown broadening and scattering broadening. The product form results because the Fourier transform of a convolution is the product of the Fourier transforms of the individual broadening functions.

RESULTS I: PURE ZINC

A. Method of Calculation

The measured quantity is the amplitude of the oscillatory torque $|C_{\rm osc}|=|\partial F_{\rm osc}/\partial\theta|$. Using Eq. (3), corrected for breadkdown by Eq. (5), and taking the derivative only with respect to the cosine term (the most rapidly varying term), we obtain

$$A_{\rm expt}=A_{\rm cal}, \tag{9}$$

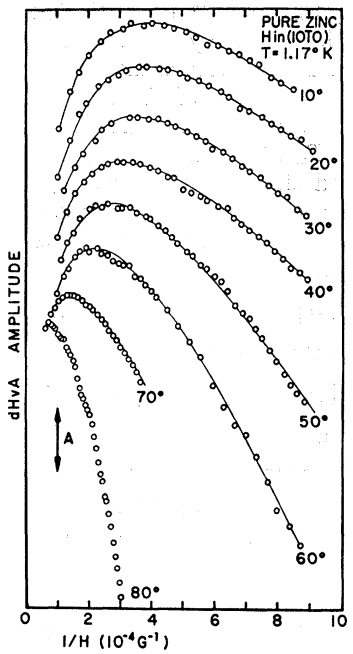

FIG. 2. Comparison of experimental dHvA amplitude for the needle oscillation [o: Eq. (12)] with best-fit-computed amplitude [curve: Eq. (13)] as a function of inverse magnetic field (in units of 10^{-4} G^{-1}) for a variety of field directions in the (10$\bar{1}$0) plane. The length A represents an amplitude increment of 0.5 in A_{expt} or A_{cal}. The curves have been arbitrarily shifted vertically for graphical clarity. If magnetic breakdown were absent, the plots would be straight lines. In all of the least-squares fits, experimental points were weighted by a factor proportional to the recorded amplitude, to avoid divergence due to amplitude uncertainty in poorly resolved oscillations.

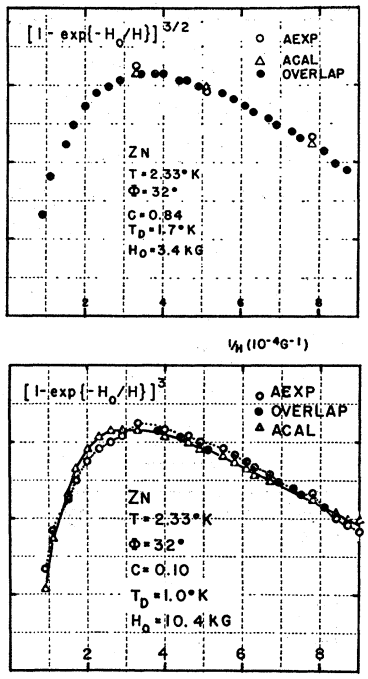

FIG. 3. Comparison of the least-squares fit obtained for identical dHvA data using (a) the Pippard formula [Eq. (8); upper curve] and (b) the Harrison formula [Eq. (10); lower curve], both as a function of $1/H$. The fit is essentially perfect in the upper curve. In the lower curve, which is also a least-squares fit, the functional form of the breakdown factor cannot adequately fit the data. Note that the least-squares value of the breakdown field H_0 depends strongly on the form of the breakdown correction: $H_0=3.4$ kG in the upper curve, but 10.4 kG in the lower curve.

where A_{expt} and A_{cal} are defined so that measured and easily computed quantities appear on the left, and unknown parameters appear on the right:

$$A_{\text{expt}} \equiv \ln\left\{C\left(\frac{1}{H}, T\right)\sinh\left(\lambda\frac{m^*}{m_0}\frac{T}{H}\right)T^{-1}H^{-1/2}\right\}, \quad (10)$$

$$A_{\text{cal}} \equiv B - \lambda\frac{m^*}{m_0}\frac{X}{H} + \frac{3}{2}\ln\left[1-\exp\left(\frac{-H_0}{H}\right)\right]. \quad (11)$$

In the absence of magnetic breakdown, a plot of A_{expt} versus $1/H$ would be a straight line of slope proportional to X. In Eqs. (10) and (11), $\lambda=\pi^2k/\mu_B$, and C is the measured torque amplitude. The effective-mass term in Eq. (11) was calculated using mass values measured[23] at fields below H_0. The three unknown parameters B, X, and H_0 are varied iteratively by a computer until a least-squares fit of Eq. (10) is obtained.[28,29] H_0 is the best value of the breakdown field, assuming Pippard's form [Eq. (5)] for the breakdown factor. X is the Dingle temperature, and must be obtained simultaneously with H_0, since a graphical determination of X at fields below H_0 will be in error for reasons described below. The constant B involves geometrical parameters of the Fermi surface:

$$B = (\text{const})(\text{volume})\frac{\partial S}{\partial\theta}\left[\frac{\partial^2 S}{\partial P_z^2}\right]^{-1/2}. \quad (12)$$

Since the shape of the needle is known, B could be calculated at any field direction, but was left as a parameter for convenience.

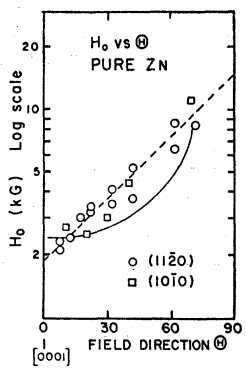

FIG. 4. Least-squares-fit values of breakdown field H_0 on a logarithmic scale in pure zinc versus magnet angle in the (11$\bar{2}$0) and (10$\bar{1}$0) crystal planes. The solid curve shows the behavior which would be expected from Eq. (2) if, as H was tilted, V_G remained constant and the component of the Fermi velocity normal to the zone face varied simply as $\cos\theta$.

[28] The iterative least-squares fit to an arbitrary function is described by J. D. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, Maryland, 1962), 15th ed., p. 539. The computer program used is described in Ref. 29.

[29] R. J. Higgins, thesis, Northwestern University, 1965 (unpublished). Available on University Microfilms #65-12, 101.

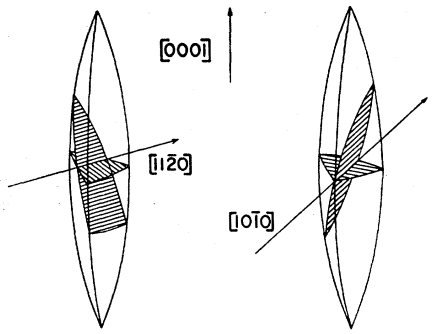

FIG. 5. Needle orbits with H at an arbitrary direction in the (11$\bar{2}$0) and (10$\bar{1}$0) reciprocal lattice planes. In the former case, as H is tilted away from [0001], all three corners of the orbit move towards the tips of the needle. In the latter case, one corner of the orbit remains centered on one edge of the needle at all angles of H. The orbit samples different regions of k space in these two cases, with potentially different values of the breakdown probability. The needle is actually more elongated than shown here, having a length-to-diameter ratio of about 16.

Higher harmonics of the dHvA amplitude have been dropped from Eqs. (10) and (11) to simplify the curve fitting. This is unquestionably justified for the alloys, where large scattering results in negligible harmonic amplitude. The pure zinc crystal used had a second harmonic amplitude of less than 30% at high fields. It can be shown[29] that a second harmonic *amplitude* of 30% changes the measured *envelope* by at most 10% and generally less, depending upon the relative phase. This is certainly negligible compared to the breakdown effects of interest, which amount to factors of 2–5.

B. Comparison of Measured and Computed dHvA Amplitude: A Test of the Pippard Theory; Angular Dependence of Breakdown Field

The results of the least-squares fit for pure zinc are shown in Fig. 2 for field directions in the (10$\bar{1}$0) plane. Essentially identical results were obtained in the (11$\bar{2}$0) plane. There is close agreement between measured points and the computed curve amplitudes at all field directions. Such a close fit is a stringent empirical test of the Pippard breakdown formula [Eq. (5)] which, as shown in Fig. 3, fits the observations better than an alternative expression [Eq. (8)]. Several other breakdown formulas were tried, but in all cases the computer calculation diverged. The best-fit values of H_0 are shown in Fig. 4 for various field directions. The values are the same in both (10$\bar{1}$0) and (11$\bar{2}$0) planes, within experimetal uncertainty. H_0 varies from 2.2 kG when H is parallel to [0001] to about 10 kG when H is 70° away from [0001].

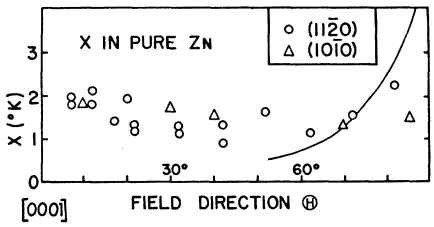

FIG. 6. Computed least-squares-fit values of the scattering temperature X in pure zinc as a function of magnetic field direction. The curve is a smoothed version of the results of Ref. 20; the scatter was about 1°K.

There is no *a priori* reason to expect a breakdown correction of the form q^3 [Eq. (5)] to be valid when H is tilted away from [0001], since not all three "corners" of the electron orbit are then equivalent (Fig. 5). A breakdown correction of the form $q_1q_2q_3$ might be more appropriate. Yet, it is clear that the data is well fit by the simpler q^3 form (Fig. 2), i.e., a single value of H_0. This observation, plus the fact that the H_0 values are indistinguishable in both planes, in spite of the differences in orbits shown in Fig. 5, requires that the band gap which rounds the corners of the needle [V_G in Eq. (2)] is essentially constant over the region of k space sampled by these measurements. The rise in H_0 as H is tilted away from [0001] is thus to be associated primarily with a decrease in the component of Fermi velocity perpendicular to the zone face.

These conclusions appear to correlate well with Stark's[12] interpretations of his galvanomagnetic measurements in zinc. Using the size of the Hall coefficient measured above H_0 and the known extremal area of the needle, Stark deduced that the breakdown field is *constant* over the *central third* of the needle, then *increases rapidly* beyond that point toward the tips. Our observation of a breakdown field with angular dependence *at all angles* of H is not in conflict with Stark's deduction, since his calculation is of the volume broken down for $H\|[0001]$, whereas our dHvA results (which sample only extremal areas) with H at arbitrary angles include additional angular dependence due to the Fermi velocity term. Moreover, the sharp rise in breakdown field which he suggests occurs in the upper and lower third of the needle would not show up in the dHvA measure-

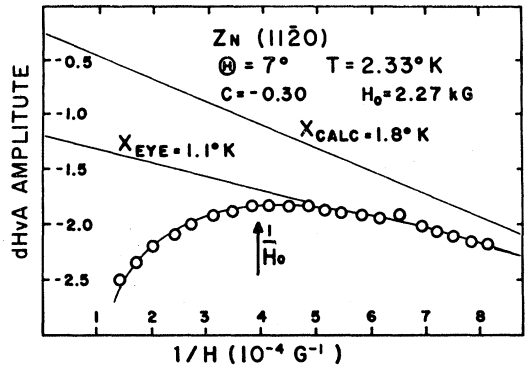

FIG. 7. An example of the difference between a low-field straight-line fit drawn by eye (X_{eye}=1.1°K) and the linear part of the least-squares fit (X_{calc}=1.8°K; the lowest curve is the full fit including the breakdown term). As explained in the text, the difference accounts in part for the discrepancy apparent in Fig. 6 between the isotropic relaxation time reported here and the anisotropic one of Ref. 20.

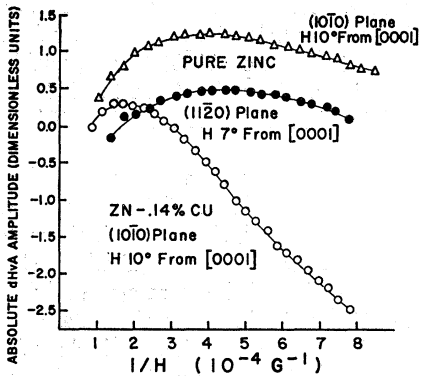

FIG. 8. An example of the effect of alloying on the absolute dHvA amplitude [Eq. (10)].

ments except at angles more than 80° from [0001], because of the elongated shape of the needle (16 to 1 length to diameter).[30] Our conclusion that V_G is constant over the region of the needle sampled by a 70° range of field directions is thus completely compatible with Stark's deduction of a constant breakdown field over the central third of the needle.

C. Isotropy of the Relaxation Time

The values of the Dingle scattering parameter X obtained from the least-squares fit are shown in Fig. 6. The values are essentially identical in the (11$\bar{2}$0) and (10$\bar{1}$0) planes. They are approximately constant ($\pm 50\%$) over the angular range, in contrast to the values from Ref. 20 (smooth curve in Fig. 6) which rise by a factor of 10 as the angle varies from 50° to 90°. Though the absolute value of X varies from sample to sample, depending on purity and past history, the angular dependence is of more interest as a measure of the k dependence of Bloch-state lifetime. Our measurements show an isotropic lifetime on the needle. The qualitative discrepancy with Ref. 20 is resolved by noting that the usual procedure of evaluating X by fitting a straight line to the linear portion of the amplitude (Fig. 3) lowers the *apparent* X value as **H** approaches [0001], because of magnetic breakdown. Breakdown gives a barely perceptible curvature to the amplitude even at fields well below H_0, which lowers the apparent slope of the linear portion, as demonstrated by Fig. 7. This effect becomes unimportant for field directions far from [0001] where H_0 becomes large. Thus, a simultaneous determination of breakdown field avoids a spurious angular dependence of the scattering parameter X.[31]

[30] 80° from [0001] the computer fit diverged, indicating that the q^3 form is no longer valid.

[31] We are informed [A. S. Joseph (private communication)] that the authors of Ref. 20 were aware of this complication and therefore did not publish X values for H near [0001].

RESULTS II: DILUTE ALLOYS

A. Observed Increase in Breakdown Field

A comparison of measured amplitudes in pure zinc and a 0.14% Cu alloy is shown in Fig. 8. Several features are apparent. The increased impurity scattering shows up as an increase in slope [increase in X in Eq. (11)] causing the low-field amplitude to be significantly smaller in the alloy crystal. Further, the downward curvature towards low $1/H$ due to magnetic breakdown

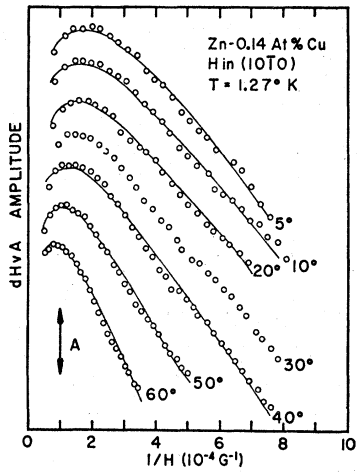

FIG. 9. Least-squares fit to the needle dHvA amplitude in a 0.14 at.% Cu alloy, with the same terminology as in Fig. 2. The length A represents an amplitude increment of 1.0.

is far less apparent in the alloy crystal, indicating an increase in the breakdown field H_0. An increase in the linear slope of Eq. (11) will of course shift the maximum in the total amplitude toward lower $1/H$. This would not account for the more nearly linear shape of the alloy curve, and in any case is taken into account in the results which follow by simultaneously varying H_0 and X in the least-squares fit. A corollary of the increase in H_0 is the unusual result apparent in Fig. 8 that the *high*-field dHvA amplitude in the *impure* system may *exceed* that in the *pure* system.

The results of amplitude measurements and curve fitting on several dilute zinc alloys, using methods identical with those of Sec. I, are shown in Figs. 9–11. A simultaneous least-squares fit allowing for variation both in X and H_0 gives the results shown in Fig. 12. H_0 increases by roughly a factor of 2 with 0.14% Cu and a factor of 4 with 0.1% Al. Also relevant is amplitude data in Zn-Mn alloys (Ref. 32: Fig. 7 compared with Fig. 8) where only 0.008% Mn almost totally removes the high-field amplitude curvature.

B. Interpretation of Breakdown Field Increase

We are led by the following qualitative arguments to reject an interpretation of this result in terms of *band-*

[32] F. T. Hedgcock and W. B. Muir, Phys. Rev. **129**, 2045 (1963).

gap changes, and instead suggest that alloying, *via impurity scattering*, diminishes the effect of magnetic breakdown on the dHvA amplitude.

(1) An increase in H_0 suggests at first an increas in the band gap $V_G(G=[11\bar{2}0])$, since $H_0 \propto V_G^2$ [Eq. (2)]. This could arise in several ways when Cu is the impurity:

(a) Pure Cu has lattice potential components[33] much larger than pure Zn, so that Cu impurities in Zn would be likely to increase the "average" value of V_G.

(b) Measurements[23] have shown that the needle cross-sectional area increases rapidly with Cu impurities, due to the combined effect of electron density and (dominant) axial ratio change. An electron orbit, therefore, samples a region of k space further from the symmetry point K than in pure zinc. Because of evidence[12] that the needle band gap is strongly position-dependent, and because the smallness of the needle band gap is due to nearness to the zero crossing of the zinc pseudopotential $V(q)$ curve, a shift in the needle band gap in an orbit whose size has been increased by alloying is not unexpected.

(2) However, the observation that Al impurities also increase H_0 effectively rules out both (a) and (b) above,

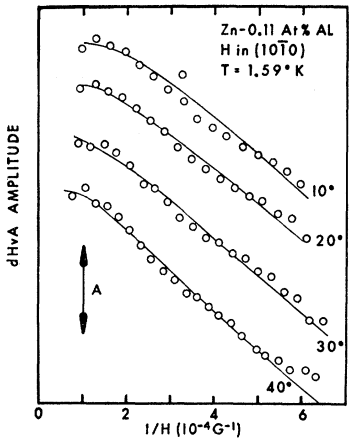

FIG. 10. Least-squares fit to the needle dHvA amplitude in a 0.11 at.% Al alloy, with same terminology as in Fig. 2. The length A represents an amplitude increment of 2.0.

since: (a) Al is a nearly-free-electron metal with small lattice potential components[34] comparable to those of zinc; (b) Al produces[23] no change in the needle orbit size because of exact compensation of electron density and axial ratio changes. These simple arguments applied to a complex band structure are not sufficient to *disprove* a connection between the observed H_0 increase and band-gap changes, but merely suggest that our indications of a cusp in H_0 plotted versus valence-electron concentration are not *likely* to be explained by band-gap arguments. This conclusion is further reinforced by the

[33] B. Segall, Phys. Rev. **125**, 109 (1962).
[34] N. W. Ashcroft, Phil. Mag. 8, 2055 (1963).

TABLE I. Correlation between increase in computed breakdown field H_0 and scattering temperature X due to alloying. Values refer to $H\|[0001]$. Results on the Zn–0.21% Cu alloy are not included for reasons discussed in connection with Fig. 11. Errors shown indicate roughly the range of values obtained rather than statistical errors. Amplitude data on the Zn-Mn alloy were taken from Ref. 32. Their measurements do not extend to high enough fields to allow us to determine H_0 unambiguously by a least-squares fit. An approximate H_0 estimate was made by comparison of their high-field curvature with a comparable field region of our 0.14% Cu data.

System	H_0(kG)	X(°K)
Pure Zn	2.2±0.3	1.5±0.5
Zn–0.14 at.% Cu	5±1	4.5±0.5
Zn–0.11 at.% Al	8±2	6.5±1
Zn–0.008 wt.% Mn	≥6[a]	5.5±0.5

[a] From Ref. 32.

observation that only 0.008% Mn,[32] which produces no detectible period change, almost totally removes the high-field amplitude curvature.

A correlation between the apparent increase in H_0 and increased *scattering* is apparent, as shown in Table I. What determines H_0 in impure systems is apparently not the valence of the impurity, but the relaxation time τ as measured by the factor $X \propto \tau^{-1}$. This qualitative conclusion needs to be verified in a further series of measurements. Tentative interpretations will now be discussed.

C. Effect of Magnetic Breakdown in the Strong Scattering (Random Phase) Limit

Referring to the assumed form for the dHvA breakdown correction [Eq. (8)], either H_0 must show a dependence on relaxation time not given by the present theory [Eq. (2)], or the q^3 form is not appropriate for

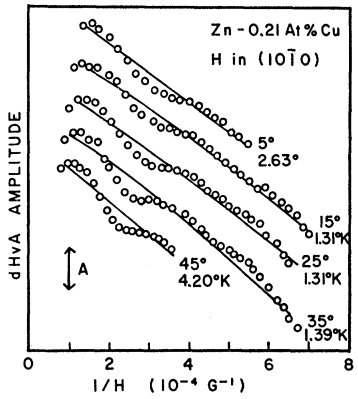

FIG. 11. Least-squares fit to the needle dHvA amplitude in a 0.21 at.% Cu alloy, with same terminology as in Fig. 2. The length A represents an amplitude increment of 1.0. The H_0 parameter values obtained from this fit are not reliable, since the data exhibit an amplitude dip in the midfield range which cannot be fit by the dHvA expression used. It was established that this midfield dip is not due to eddy current torques while field sweeping, nor to field calibration errors, nor to crystalline substructure. Inhomogeniety of alloy composition is possible and, because of the composition dependence of dHvA period, would give a beating effect in the dHvA amplitude.

impure systems. The evidence presently available supports the latter suggestion, though not ruling out the former. The derivation[10,14,15] of the q^3 form for the dHvA breakdown correction [Eq. (5)] is based upon a network of quasiparticle orbits coupled in a *phase-coherent* way, making use of a complex breakdown probability amplitude p and phase matching at junctions of the network. Pippard points out in a later paper[35] that phase coherence of the entire network is unlikely even in the pure metal, because of the presence of dislocations in the lattice which act as scattering centers, randomizing the phase information carried on the larger orbits. He uses this idea in an attempt to account for a factor of 10 discrepancy between the observed[12] magnitude of the magnetoresistance oscillations in zinc and the magnitude calculated[10] using the phase-coherent coupled orbit model. We suggest that in the limit of strong *impurity* scattering, as in these zinc alloys, the q^3 breakdown correction to the dHvA amplitude is not appropriate. An alternative approach is to treat the electron lifetime in an orbit which suffers magnetic breakdown as a simple scattering problem.

Brailsford[27] has shown recently that the exponential form of the scattering factor in the dHvA amplitude [Eq. (3)] does not require the assumption[19] of a Lorentzian line shape for the Landau levels, but requires only the definition of the lifetime τ of the state. If magnetic breakdown can be treated as a simple scattering process, the breakdown scattering probability on the needle per unit time $1/\tau_b$ is likely to be of the form[36]

$$1/\tau_b=\left(\frac{\text{scattering probability}}{\text{orbit corner}}\right)\left(\frac{\text{orbit corner}}{\text{orbit}}\right)\left(\frac{\text{orbit}}{\text{time}}\right)$$
$$=3(\omega_c/2\pi)\exp(-H_0/H), \qquad (13)$$

and writing the net scattering probability per unit time as $(1/\tau_s+1/\tau_b)$, where τ_s is due to impurity scattering and τ_b is due to magnetic breakdown, the generalized scattering factor is of the form[36]

$$\exp[-\pi/\omega_c\tau-\tfrac{3}{2}\exp(-H_0/H)]. \qquad (14)$$

An expression of this form is qualitatively appropriate to explain the anomalous alloying results, as shown in Fig. 13. Using $H_0=2.2$ kG ($H\|[0001]$) evaluated for pure zinc in Eq. (14) results in far less high-field amplitude curvature than the q^3 form. No maximum is apparent, rather than the strong maximum of the q^3 form.[37] This is qualitatively the behavior observed in the alloys [Figs. 8–11], and is an alternative explanation for the apparent increase in H_0 obtained when the alloy data is fit by the q^3 form [Fig. (11)]. This conclusion will not be made quantitative at present, since

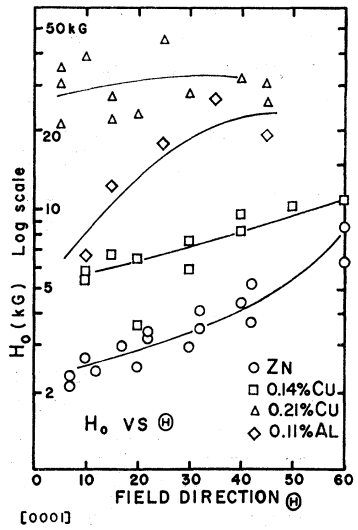

FIG. 12. Least-squares-fit values of H_0 in zinc compared to values in several dilute Zn-Cu and Zn-Al alloys, plotted on a logarithmic scale.

(1) The assumed form [Eq. (13)] for the breakdown scattering probability needs to be justified, and certain logical inconsistencies removed. For example, the dHvA amplitude of the needle does not vanish at high field in this model, even though the orbit is totally broken down.

(2) It is not clear how to go between the phase-coherent q^3 limit and the random-phase limit of Eq. (14). The validity of the simple scattering approach is likely to depend on the number of orbits per collision being small. This number is field-dependent ($=\omega_c\tau$), such that the simple scattering approach is valid to progressively higher fields as the impurity concentration ($\propto 1/\tau$) is raised. This is in line with the observed increase in H_0 values in alloy data fitted by the q^3 breakdown correction.

(3) The few alloy compositions on which measurements were made are not sufficient to establish quantitatively the scattering dependence of magnetic breakdown as seen in the dHvA effect.

[35] A. B. Pippard, Proc. Roy. Soc. (London) **A287**, 165 (1965).

[36] J. H. Condon (private communication). Prior to the experiments discussed in the present paper, Condon suggested a breakdown correction of this form, and demonstrated (unpublished) that the anomalous dHvA field dependence in zinc found by Dhillon and Shoenberg (Ref. 3) could be roughly fit by a correction of the form of Eq. (14). We later found that a correction of this form, though qualitatively correct, did not fit our experimental data well in *pure* zinc; in fact, the computer-fitting calculation diverged. As discussed in Sec. I, the q^3 form breakdown correction fit the data very well, and, in the *pure* material, has a firmer theoretical foundation than Eq. (14). Our application of Eq. (14) to explain the anomalous alloying results rests on an *assumed* form [Eq. (13)] for the breakdown scattering probability in the random-phase limit.

[37] The difference is essentially due to the following: The breakdown scattering probability per unit time, Eq. (13), approaches a limit of $3\omega_c/2\pi$ at high fields, which means that an electron completes $\frac{1}{3}$ orbit before being scattered. The q^3 breakdown correction, on the other hand, becomes very large at high fields, which means that it is extremely unlikely for an electron to complete a full orbit. Application of either of these to the high-field limit is of dubious validity, however, because neither the Pippard network model nor the Brailsford scattering formula is valid in the quantum limit.

CONCLUSIONS

The anomalously low amplitude at high magnetic fields of the dHvA oscillation of the needle orbit in zinc has been interpreted as magnetic breakdown. A breakdown correction factor derived by Pippard has been shown to fit the data very closely, providing strong support for his coupled network model. Values of the breakdown field H_0 were calculated by a least-squares method for field directions ranging from nearly parallel to nearly perpendicular to [0001]. The observations that the q^3 breakdown correction factor fits the data well for angles up to 70° from [0001], and, in addition, identical values of H_0 are obtained for H in both the $(11\bar{2}0)$ and $(10\bar{1}0)$ plane have been interpreted as evidence that the lattice band gap is essentially constant over the central third of the needle. Calculated values of the Dingle scattering temperature showed no angular anisotropy, within experimental error. This conflicts with the anisotropy found by Joseph and Gordon, but the conflict has been resolved by noting that breakdown effects persist to quite low fields and lower the apparent slope of the dHvA amplitude.

The high-field dHvA amplitude observed in several dilute zinc alloys shows considerably less curvature than found in pure zinc. When these data were fitted by a q^3 breakdown correction, apparent H_0 values 2–10 times higher than pure zinc were found. Although a number of arguments can be presented interpreting an increase in H_0 as an increase in the lattice band gap, none of these arguments were found to be consistent with a sharp H_0 increase due to impurities of both higher (Al) and lower (Cu) valence. It was suggested that the use of the Pippard q^3 breakdown correction is of doubtful validity in an impure system, since it was derived using a phase-coherent network which is unlikely in the presence of strong impurity scattering. An alternative breakdown correction was suggested, based on a generalization of the Dingle scattering factor due to Brailsford, using a breakdown scattering probability originally suggested by Condon. It was shown that this results in a high-field amplitude similar to that observed in the alloys, without requiring a major change in the breakdown field H_0. This qualitative conclusion should be confirmed in two ways. First, further amplitude measurements should be made with a wide range of alloy compositions, to confirm the apparent correlation between scattering (as measured by the scattering temperature X and by resistivity) and the high-field dHvA amplitude curvature. Transition-metal impurities such as Mn, which scatter electrons far more strongly than polyvalent metal impurities such as Cu or Al, should be used so that the measurements can be made on very dilute alloys, avoiding the complication of band-structure changes. Second, our heuristic breakdown "scattering" correction in the random-phase limit needs to be justified, so that the connection with the Pippard q^3 breakdown function becomes apparent as impurity scattering is reduced.

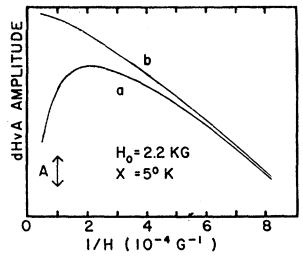

FIG. 13. Calculated dHvA amplitude. (a): Breakdown correction of the q^3 form [Eq. (5)] used in Sec. I and appropriate in the coupled orbit limit. (b): Breakdown correction using a scattering probability of the form of Eq. (13) in a scattering correction factor of the Dingle-Brailsford form as in Eq. (14), appropriate to the random-phase (strong impurity scattering) limit. The length A corresponds to an amplitude change of 0.5. A Dingle temperature of 5°K was used to make the result comparable to Zn–0.14% Cu data (Fig. 8). A breakdown field value of 2.2 kG was used in *both* (a) and (b), the value obtained at field directions near [0001] in *pure* zinc (Fig. 4). It is apparent that curve (b) qualitatively resembles the alloy results (Figs. 8 and 9), showing little high-field curvature.

ACKNOWLEDGMENTS

We are grateful to J. H. Condon, A. B. Pippard, L. Falicov, R. W. Stark, W. L. Gordon, D. H. Whitmore, J. W. McClure, and J. P. Van Dyke for helpful discussion at various stages of the work. The Northwestern University Computing Center provided several hours of computer time and helpful programming advice. These experiments were carried out at Northwestern University. The writing of this paper was carried out principally at the University of Oregon, with the support of the National Science Foundation.