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Topology of the Fermi Surface of Zinc from Galvanomagnetic Measurements

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High-field magnetoresistance and Hall effect measurements have been made on high-purity single crystals of zinc at 4.2°K in magnetic fields up to 18kG. For an arbitrary field direction there is an equal number of electrons and holes but at special field directions there are open orbits. There is clear evidence that magnetic breakdown occurs at points H and K of the Brillouin zone at quite low fields. The topology of the multiply connected sheet of the Fermi surface is similar to that predicted by the free-electron model.

INTRODUCTION

THERE has been much recent interest in the Fermi surface of zinc. Measurements of the deHaas–van Alphen effect,[1] magnetoacoustic attenuation,[2] cyclotron resonance,[3] and anomalous skin effect,[4] as well as a calculation of the band structure,[5] agree as to the basic shape and size of the surface but information about its topology, supplied by high-field galvanomagnetic measurements, is missing.

Although there have been several papers published on the galvanomagnetic effects in zinc,[6–10] the data are still insufficient to give a satisfactory description of the topology. It is the purpose of this research to obtain and interpret a complete set of galvanomagnetic measurements.

The basis for the interpretation of the high-field galvanomagnetic effects has been supplied by Lifshitz *et al.*[11,12] and can be summarized as follows[13]:

A. When only closed orbits exist and the number of holes does not equal the number of electrons ($n_e \neq n_h$), the magnetoresistance saturates for all directions of the magnetic field and current. The Hall coefficient R is related to the Fermi surface by the expression $R=(\Delta nec)^{-1}$, where $\Delta n = n_e - n_h$.

B. When only closed orbits exist and $n_e = n_h$, the magnetoresistance rises quadratically with the magnetic field for all directions of field and current except for $H\|J$, where it saturates. The transverse even voltage is large relative to the Hall voltage, but neither effect is related in a simple way to the shape of the Fermi surface.

C. When the Fermi surface is multiply connected and permits open trajectories with a single average direction, the magnetoresistance is quadratic in the magnetic field and depends upon the current direction as

$$\Delta\rho/\rho = a + bH^2\cos^2\alpha, \qquad (1)$$

where a and b are constants and α is the angle between the current direction and the direction of open orbits. The Hall coefficient is a constant but cannot be directly related to the shape of the Fermi surface.

D. When the Fermi surface is multiply connected and permits more than one direction of open orbits, the magnetoresistance saturates for all directions of the current as in case A, but now the Hall coefficient is proportional to H^{-2}.

An invaluable aid to the interpretation of the galvanomagnetic measurements, as well as the other techniques reported in references 1 to 4, has been the free-electron model. The evidence for zinc indicates that this model gives an excellent first approximation to the Fermi surface and needs only small modifications to fit the experimental data. Diagrams of all the bands predicted can be found in references 1 and 2, and of the first and second bands of holes plus the third band "needles" in Fig. 1. Although there are four different bands in zinc only the multiply connected hole surface of the second band supports open orbits, and it is this band that is considered in most of the interpretation of the data.

EXPERIMENTAL PROCEDURE

A. Sample Preparation and Mounting

Single crystals were cut with an acid-string saw from boules prepared by the Bridgman method.[14] They were then lapped with acid until they were approximately 15 mm long and had a square cross section, about 2–3 mm on a side. The orientation of the samples was determined by x rays and the crystal axes[15] were aligned to

[1] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 489 (1962).
[2] D. F. Gibbons and L. M. Falicov (to be published).
[3] J. K. Galt and F. R. Merritt, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 159.
[4] E. Fawcett, J. Phys. Chem. Solids **18**, 320 (1961).
[5] W. A. Harrison, Phys. Rev. **126**, 497 (1962).
[6] B. G. Lazarev, N. M. Nakhimovich, and E. A. Parfenova, Zh. Eksperim. i Teor. Fiz. **9**, 1169 (1939).
[7] E. S. Borovik, Doklady Akad. Nauk. S.S.S.R. **70**, 4 (1950).
[8] E. S. Borovick, Zh. Eskperim, i Teor. Fiz. **30**, 262 (1956) [translation: Soviet Phys.—JETP **3**, 243 (1956).]
[9] C. A. Renton, in *Proceedings of the Seventh International Conference on Low-Temperature Physics*, (University of Toronto Press, Toronto, 1960), p. 153.
[10] E. Fawcett, Phys. Rev. Letters **6**, 534 (1961).
[11] I. M. Lifshitz, M. I. Azbel, and M. I. Kaganov, Zh. Eksperim. i Teor. Fiz. **31**, 63 (1956) [translation: Soviet Phys.—JETP **4**, 41 (1957)].
[12] I. M. Lifshitz and V. G. Peschanskii, Zh. Eksperim. i Teor. Fiz. **35**, 1251 (1958) [translation: Soviet Phys.—JETP **8**, 875 (1959)].
[13] W. A. Reed and J. A. Marcus, Phys. Rev. **126**, 1298 (1962).

[14] The zinc (99.999% pure) was obtained from the N. J. Zinc Company and then zone refined before fabricating into single crystals. The residual resistance ($R_{290°K}/R_{4.2°K}$) of the samples varied from 15 000 to 20 000.
[15] Zinc has a hexagonal-close-packed structure.

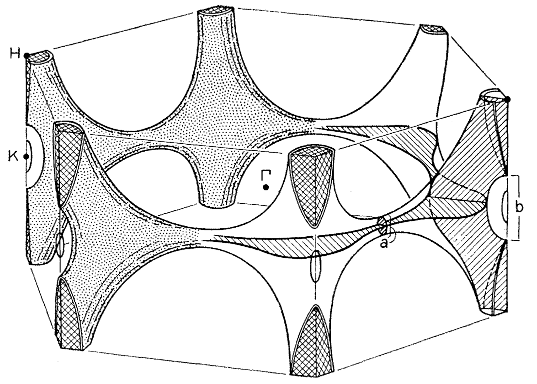

FIG. 1. First and second bands of holes plus third band of electrons (needles) of the Fermi surface of zinc.

within 1 deg of the sample axes. Three pairs of mutually perpendicular potential leads were soldered to each sample so all components of the electric field could be measured. The Hall (transverse) leads were placed in a plane perpendicular to the sample axis and the magnetoresistance leads were placed above and below the Hall leads and were separated by about 6 mm. The crystal was mounted on a Bakelite disk such that the sample and disk could be attached to or removed from the sample assembly without disturbing the sample or the leads connected directly to it.

The sample assembly was constructed so that it could be clamped to the Dewar tail and the crystal rotated $\pm 5°$ about one horizontal axis and $\pm 90°$ about a horizontal axis perpendicular to the first. In this way, a sample could be accurately aligned in the magnetic field and rotated from a vertical to a horizontal position while the sample was immersed in liquid helium.

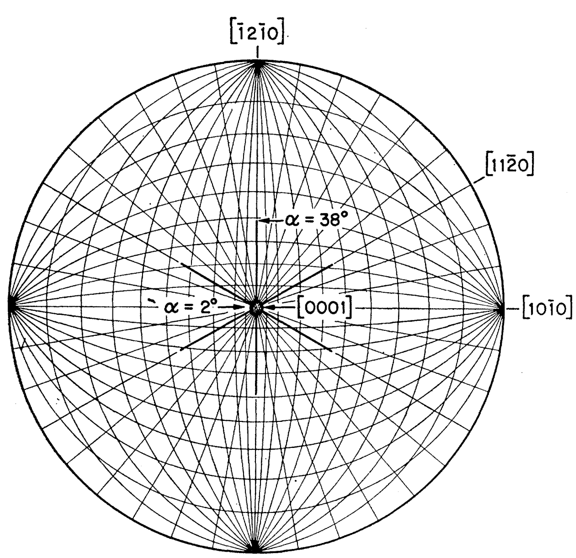

FIG. 2. Stereogram of the magnetoresistance of zinc. Thin lines indicate planes of magnetic field rotation; thick lines indicate one-dimensional regions of open orbits; central circle indicates two-dimensional region where magnetoresistance saturates.

B. Measurement Techniques

The potentials were measured with a Keithley Model 149 milli-microvoltmeter and recorded as continuous functions of either magnetic field strength or direction on a Moseley Model 2S *x*-*y*-recorder. Encoders were attached to both the *x* and *y* axes and their output recorded on punched paper tape by a Datex recording system. The data on the tape were then reduced by an IBM 7090 computer and the final results automatically plotted on microfilm.

The standard procedure of reversing both current and field was used to make the measurements. Thus, when the data were combined in the appropriate way the constant (even in current and field) and induced (even in current but odd in field) potentials were removed.[16]

A series of rotation curves were taken at 4.2°K on all

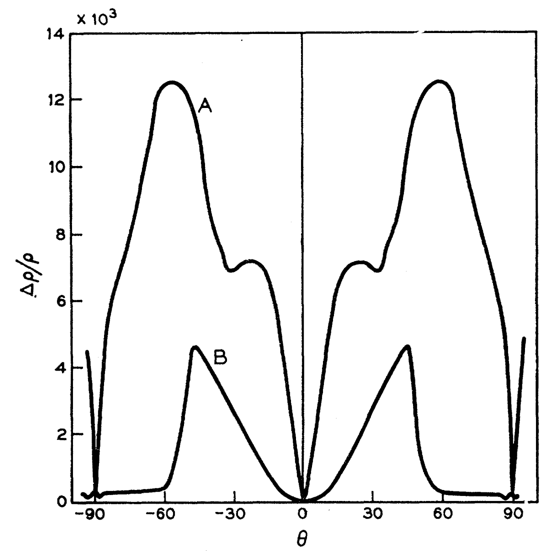

FIG. 3. Magnetoresistance rotation curves for zinc at 4.2°K, $H=18$kg, $J\|[11\bar{2}0]$. Curve A: transverse rotation, $H\|[10\bar{1}0]$ at $\theta=0°$. Curve B: Longitudinal rotation, $H\|J$ at $\theta=0°$, $H\|[0001]$ at $\theta=90°$.

three potential pairs with the magnetic field transverse to the current and with the sample tipped in 10° intervals about each of the crystal axes perpendicular to the current. At various field directions which appeared interesting on the rotation curves, the field dependence of the three pairs was measured. This procedure was followed for the current along three major crystallographic axes so that all the field directions which give rise to open orbits could be found.

RESULTS AND DISCUSSION

The magnetoresistance data are summarized on the stereogram (Fig. 2). The light lines indicate the planes in which the rotation curves were taken; the heavy

[16] For more details see reference 13.

lines show field directions where saturation of the magnetoresistance was observed, and the circular shaded region around the [0001] axis is a two-dimensional region of saturation. The one-dimensional "whiskers" extend in the ⟨11$\bar{2}$0⟩ directions out to $\alpha=38°$ (α is the polar angle measured from the [0001] axis) and the radius of the two-dimensional region is $\alpha=2°$.

A typical transverse magnetoresistance rotation curve for H in the (11$\bar{2}$0) plane is shown in Fig. 3, curve A. The magnetoresistance is large for all field directions and quadratic in the field except at the bottoms of the deep minima where it saturates. The general quadratic dependence indicates that for most field directions the number of holes equals the number of electrons ($n_e=n_h$). This is as expected since the electrons that overlap into the third and fourth bands leave an equal number of holes in the first and second bands. Curve B is a longitudinal rotation curve for the field in the (10$\bar{1}$0) plane. The minimum at $\theta=0°$ is due to the field being parallel to the current, but the broad minima at $\theta=\pm 90°$, which define the "whiskers" shown in Fig. 2, are due to open orbits in the basal plane whose origin will be discussed later.

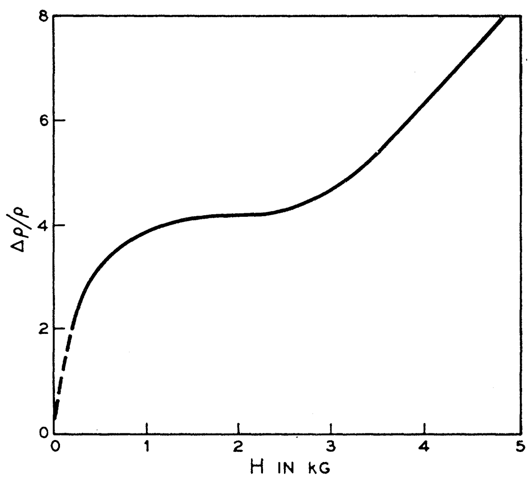

FIG. 4. Magnetoresistance field dependence curve for zinc at 4.2°K. J∥[11$\bar{2}$0], H∥[10$\bar{1}$0].

The field dependence was measured at $\theta=0°$ on curve A, of Fig. 3, and is shown in Fig. 4. Although this curve was taken for J∥ [11$\bar{2}$0] and H∥[10$\bar{1}$0], it is typical of the transverse magnetoresistance whenever the current and field are both in the basal plane. The initial saturation observed at $H<3$kG is expected since the Fermi surface permits open orbits parallel to the hexagonal axis[17] (see Fig. 1). However, one would normally expect this saturation to continue up to the higher fields so the advent of a quadratic behavior at $H>3$kG needs further explanation.[18] Cohen and Falicov[19] have shown that, due to spin-orbit coupling in the hcp metals, there is an energy gap at symmetry point H. However, this gap is quite small so that at attainable magnetic fields "magnetic breakdown"[20] will occur and the carriers will jump the gap. The original double zone scheme proposed by Harrison[21] is then applicable and the open orbits that are parallel to the hexagonal axis in the single zone scheme no longer exist.

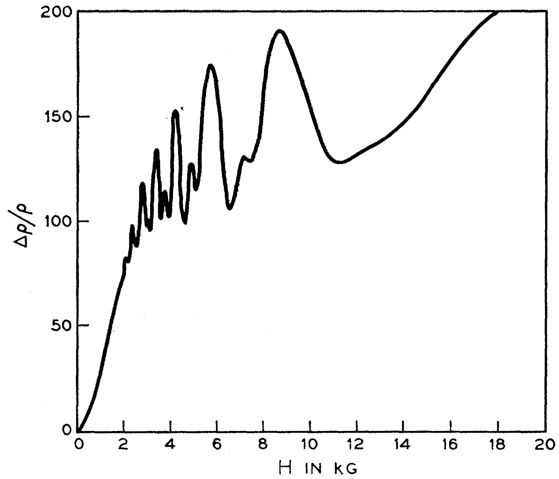

FIG. 5. Magnetoresistance field dependence curve for zinc at 4.2°K. J∥[11$\bar{2}$0], H∥[0001].

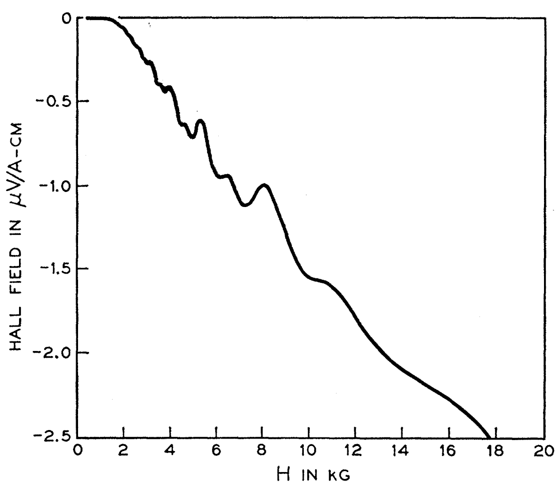

FIG. 6. Hall effect field dependence curve for zinc at 4.2°K. J∥[11$\bar{2}$0], H∥[0001].

[17] That this saturation is associated with open orbits parallel to the hexagonal axis is confirmed by the quadratic variation of the magnetoresistance when the field is in the (0001) plane but J∥[0001] [see Eq. (1)].

[18] Considerable effort was spent checking this curve to be certain that the change in field dependence was not due to twisting of the sample in the field. Because a field dependence curve plotted from the minima of a series of rotation curves taken at different field intensities is identical to curves taken by fixing the field direction and varying the intensity, there is now no doubt about the validity of Fig. 4.

[19] M. H. Cohen and L. M. Falicov, Phys. Rev. Letters **5**, 544 (1960).

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

[21] W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

When the number of open orbits becomes negligible due to breakdown, there is compensation of electrons and holes and the magnetoresistance will become quadratic in the field.

The probability that a carrier will jump the gap during one pass through the breakdown region is given by[22]

$$P=\exp(-\pi m^* c E_g^2/8\hbar e H E_F),$$

so that the probability of a carrier remaining on an open orbit after passing through n regions is $(1-P)^n$. If we assume $m^*=m_0$, $E_F=9.9$ eV, $n\sim30$ and $E_g=2.74\times10^{-2}$ eV,[19] the transition probability will equal $1/e$ at $H\approx2.5$ kG and the probability of an orbit remaining open is about $(1-1/e)^{30}\approx10^{-5}$. Considering the approximations used in estimating the breakdown probability, the experimental results are in agreement with Cohen and Falicov's estimate of the gap. Harrison[5] also concluded from his theoretical calculations and the deHaas–van Alphen measurements of Joseph and Gordon[1] that breakdown must occur.

Figure 5 shows the field dependence of the magnetoresistance at $\theta=90°$ on curve A, Fig. 3, $[J\|[11\bar{2}0]$, $H\|[0001]]$. The oscillations observed (Schubnikov–deHaas effect) have the same period as the deHaas–van Alphen effect reported by Joseph and Gordon[1] and arise from the needles in the third band located at point K. The monotonic part of this curve is quadratic at low fields[23] but saturates at the highest fields. Since the field is along a sixfold axis, symmetry arguments prohibit open orbits so the saturation of the magnetoresistance must be due to the loss of compensation ($n_e\neq n_h$) or "discompensation."

There are two different possibilities for discompensation for this field direction. The first is called "geometric discompensation" since it is a result of the geometric shape of the Fermi surface. Baratoff[24] has shown that when the height of the horizontal arms of the "monster" is greater than the height where the "tentacles" are *not* in contact with the zone edge ($a>b$ in Fig. 1), there is a range of planes perpendicular to the k_c axis where the hole orbits rearrange themselves into electron orbits and n_e no longer equals n_h. The thickness of this discompensation region can be calculated from a measurement of the Hall voltage by the equation,

$$d=4\pi^3/ARe,$$

where R is the Hall coefficient, A is the cross-sectional area of the Brillouin zone in the (0001) plane, and e is the charge of the electron.

The alternative explanation for discompensation when the field is along the hexagonal axis is magnetic breakdown. Cohen and Falicov[20] have shown that in Mg the band gap between the second and third bands near point K is small so that at high enough fields the electrons will jump this gap and will follow orbits corresponding to the free-electron sphere. This effect has been observed experimentally in Mg by Priestly[25] in the high-field deHaas–van Alphen effect and by Stark *et al.*[26] in the magnetoresistance. For the case of magnetic breakdown a measure of the height of the breakdown region can be calculated from the Hall coefficient by the equation,

$$d'=4\pi^3/2ARe.$$

The field dependence of the Hall effect for $H\|[0001]$ is shown in Fig. 6. The Hall effect is essentially zero up to about 1.3 kG and then starts to increase rapidly. The oscillations superimposed on the monotonic curve have the same origin as the oscillations seen in the magnetoresistance. A calculation of the Hall coefficient at the highest fields used gives $R=7.6\times10^{-3}$ emu which corresponds to a geometric discompensation thickness of $d=0.158$Å^{-1} or alternatively a breakdown thickness of $d'=0.079$Å^{-1}.

The d's calculated give a basis for deciding between the two types of discompensation. The free-electron model gives the height of the horioznatal arms (a) as 0.423Å^{-1} and the height along the zone edge (b) as 0.342Å^{-1} or a value $d=a-b=0.081$Å^{-1}. This value of d can be considered as an upper limit since any deviation from the free-electron model is likely to increase b and decrease a. The experimental results of Joseph and Gordon[1] show that the cross-sectional area of the horizontal arms is smaller by a factor of 10 than that predicted by the model which means that the top of these arms has probably shrunk below the contact point at the zone edge. Thus, geometrical discompensation is not a satisfactory explanation in the light of the experimental evidence.

By postulating that magnetic breakdown occurs when H is parallel to the c axis, a more reasonable explanation can be constructed. The observed height of the breakdown region is 0.079Å^{-1}, about one-third the height of the needles[27] (0.232Å^{-1}), which is reasonable from a theoretical point of view. The field dependence of the magnetoresistance and Hall effect support this mechanism. At low fields ($H\lesssim1.3$ kG) there is no breakdown and zinc appears to be a compensated metal with a quadratic magnetoresistance and a small Hall effect. At fields greater than about 1.3 kG breakdown begins, n_e no longer equals n_h, and the magnetoresistance saturates. The Hall effect then becomes large with $R\sim(\Delta n)^{-1}$. The "whiskers" seen on the stereogram are due to open orbits in $\langle10\bar{1}0\rangle$ directions. These are the "*ee*" orbits shown in Fig. 7, which run along one horizontal arm, pass above

[22] E. I. Blount, Phys. Rev. **126**, 1636 (1962).
[23] Even at the lowest fields used, $\omega_c\tau\gg1$ for all carriers.
[24] A. Baratoff (private communication).

[25] M. G. Priestley, reported by D. Shoenberg, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 80.
[26] R. W. Stark, T. G. Eck, W. L. Gordon, and F. Moazed, Phys. Rev. Letters **8**, 360 (1962).
[27] This dimension was calculated using data reported in reference 1 by assuming the needles are ellipsoids of revolution.

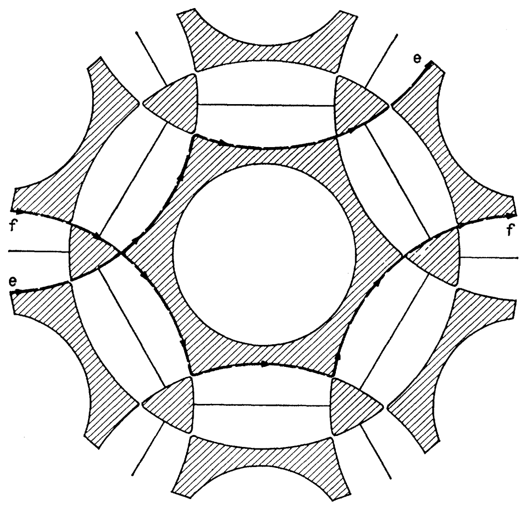

FIG. 7. Open orbits in the basal plane which result from magnetic breakdown [after Stark *et al.* (see reference 26)].

the breakdown region at the zone edge, along the second horizontal arm and into the next zone by passing into the breadkown region and jumping the gap. The open orbits labeled "*ff*" in Fig. 7 are not observed outside of the two-dimensional region of the stereogram. This is because the horizontal arms of the monster in Zn are about 5 times smaller than in Mg and cannot support this orbit for $\alpha > 2°$.

CONCLUSIONS

The conclusions drawn from the galvanomagnetic measurements on zinc at 4.2°K can be summarized as follows:

1. For an arbitrary field direction zinc has an equal number of electrons and holes.

2. At least one sheet of its Fermi surface is multiply connected.

3. The topological features are in agreement with the modified free-electron model if one takes into account magnetic breakdown occuring at two places on the Fermi surface. The first is near point H on the hexagonal faces of the Brillouin zone when the field is perpendicular to the [0001] axis. The second is near point K of the zone when the field is parallel to the hexagonal axis where the orbits around the outside of the monster and the needles break down in giant "free-electron" orbits. The height of this breakdown region is $0.079 Å^{-1}$.

4. Open orbits in the (0001) plane exist as a result of the magnetic breakdown near K. Open orbits in the basal plane which cannot be attributed to breakdown have not been observed.

Note added in proof: Recent work by Stark [Phys. Rev. Letters **9**, 482 (1962)] confirms our conclusion about magnetic breakdown near point K. There is, however, apparent disagreement on the "whiskers" shown on the stereogram. This appears to be only a difference in our definitions of where open orbits end. We have used the angles where the quadratic field dependence ceases and the magnetoresistance saturates at the highest fields, whereas Stark seems to have used the angle where the magnetoresistance first starts to decrease more rapidly on a rotation curve while still retaining a quadratic field dependence [see Fig. 3(B)].

Stark has also suggested (private communication) that the lack of complete saturation in Fig. 4 is a result of the current not being exactly perpendicular to the [0001]-axis. As can be seen from Eq. 1, if B is very large and α is not exactly 90°, it is possible for the quadratic term to become larger than the constant term. We rechecked our measurements on a sample ($R_{290°K}/R_{4.2°K} = 19\,400$) prepared by cleaving, and again observed the change from saturation to quadratic field dependence. With x rays we determined that the angle between the current direction and [0001] axis was $90° \pm 5'$ whereas using Eq. (1) and reasonable values of A and B we would require $\alpha \approx 84°$. Hall measurements made for $H \perp [0001]$ also indicate breakdown. Theory predicts that the Hall voltage depends only on the field direction and should be a linear function of the field in the case of open orbits.[12] We find that the Hall voltage departs markedly from linearity when $H \perp [0001]$. These results provide additional support for our conclusion that magnetic breakdown occurs near point H of the Brillouin zone.

ACKNOWLEDGMENTS

We would like to thank J. H. Wernick and P. H. Schmidt for zone refining and growing the single crystals. We would also like to thank E. Fawcett for many helpful discussions on the interpretation of the results.

APPENDIX: TRANSVERSE EVEN VOLTAGE

In reference 13, Appendix A, Reed and Marcus discussed the transverse even voltage of gallium. They found that this voltage was large even in well-aligned crystals and they questioned whether it would go to zero as required by symmetry, when the current was along a crystal axis and the field was in a plane perpendicular to the current.

In our measurements, we were able to make small adjustments of the cyrstal in the field at 4.2°K and we found that, when the crystal was accurately aligned, the transverse even voltage became quite small and in some cases zero. From these results we now conclude that the transverse even voltage is very dependent on the alignment of the crystal in the field but does not violate the restrictions on its existence imposed by symmetry.