Hall Effect in Zinc Crystals at Low Temperatures*

JOHN K. LOGAN † AND JULES A. MARCUS Department of Physics, Northwestern University, Evanston, Illinois (Received September 3, 1952)

An experimental study has been made of the Hall effect in single crystals of zinc. For each crystal, one component of the Hall field was measured for a fixed crystallographic orientation of the current density, but for various orientations of the magnetic field in the plane perpendicular to the current density. At 77°K, the Hall field is a linear function of magnetic field which can be characterized by two coefficients. The first coefficient, for the interaction between the magnetic field component parallel to the hexagonal axis and current density component in the hexagonal plane, has a value of about 2×10^{-12} ohm cm/gauss. The second coefficient measures the interaction between the magnetic field component in the hexagonal plane and the current density component perpendicular to this field component. Its value is about 0.2×10^{-12} ohm cm/gauss At 20.4°K, the Hall field is nonlinear with magnetic field. For some orientations, the measured component of the Hall field increased with increasing magnetic field. In other cases, the opposite behavior was observed. Between 5 and 10 kilogauss, the Hall effect is of the same order of magnitude at 20.4°K as at 77°K. No correlation was apparent between Hall effect and either susceptibility or magnetoresistance.

I. INTRODUCTION

 $S\,^{\rm TUDIES}$ of the magnetic susceptibility and magnetoresistance have indicated that at low temperatures the electronic structure of zinc may be noticeably affected by an applied magnetic field of a few thousand gauss.¹⁻⁵ If the de Haas-van Alphen effect and the irregularity in magnetoresistance can be attributed to the variation with magnetic field of the density of states near the Fermi energy, then it might be expected that the dependence of Hall effect upon magnetic field would be related to the susceptibility or magnetoresistance. There is experimental evidence that this may be true



Dewar D, and magnet Current leads are indicated by the heavier lines, potential leads, by the lighter.

* Part of a dissertation submitted to the Graduate School of Northwestern University by John K. Logan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† AEC Predoctoral Fellow, now at Naval Research Laboratory, Washington, D. C.

Washington, D. C. ¹ J. A. Marcus, Phys. Rev. **76**, 413 (1949). ² L. Mackinnon, Proc. Phys. Soc. (London) **B62**, 170 (1949). ³ Lazarev, Nakhimovich, and Parfenova, J. Exptl. Theoret. Phys. (U.S.S.R.) **9**, 1169, 1182 (1939). ⁴ Lazarev, Nakhimovich, and Parfenova, Compt. rend. acad. sci. U.R.S.S. **24**, 855 (1939). ⁵ N. M. Nachimovich, J. Phys. (U.S.S.R.) **6**, 111 (1942).

for bismuth.^{6,7} To examine this possibility further an experimental study has been made of the Hall effect in zinc single crystals.

In discussing galvano-magnetic effects in anisotropic media, it is necessary to adopt clear definitions to distinguish between the Hall effect and the magnetic change of resistance. For most isotropic substances at room temperature, the relation between electric field E and current density J can be written

$$\mathbf{E} = \rho \mathbf{J} + R \mathbf{B} \times \mathbf{J},\tag{1}$$

where ρ is the resistivity, and R the Hall coefficient characteristic of the material. If the magnetic field B is zero, the electric field is parallel to the current density. The effect of the magnetic field is to add to the ohmic field $\rho \mathbf{J}$, a Hall field $R\mathbf{B} \times \mathbf{J}$, perpendicular to both magnetic field and current density.

In defining the Hall field for cases to which Eq. (1) does not apply, some, but not all, of the properties of $R\mathbf{B} \times \mathbf{J}$ can be retained. A choice must be made of the most "characteristic" properties. Thus, the Hall field *might* be defined as E(B) - E(B=0). With this convention, the Hall field is not necessarily perpendicular to either **B** or **J**, nor does it necessarily change sign if **B** is changed to -B. Most conventions agree that the Hall field vanishes if $\mathbf{B} = 0$.

We have chosen to define the ohmic field as $\frac{1}{2} [E(B)]$ $+\mathbf{E}(-\mathbf{B})$ and the Hall field as $\frac{1}{2}[\mathbf{E}(\mathbf{B})-\mathbf{E}(-\mathbf{B})]$. Thus, the Hall field reverses its direction on reversing the magnetic field, while the ohmic field does not. Neither field changes its magnitude in this process. If $\mathbf{B} = 0$, the Hall field is zero. These properties are mathematical consequences of our definition. They are also properties of the Hall field of Eq. (1).

Another definition which is sometimes used is based on the special experimental situation in which two potential probes are attached to a conductor so as to be on an equipotential surface in the absence of a magnetic field.

⁶ A. N. Gerritsen and W. J. de Haas, Physica 7, 802 (1940). ⁷ Gerritsen, de Haas, and van der Star, Physica 9, 241 (1942).

If a magnetic field is turned on along the direction perpendicular to the current direction and the line between the potential contacts, any potential difference between the probes is called a Hall voltage. For an anisotropic substance in which the ohmic field is a noticeable function of magnetic field strength, this convention may lead to a discussion of the "quadratic" Hall effect which does not reverse sign on reversing the magnetic field. On the basis of our definitions, such a quadratic effect would be considered as magnetoresistance rather than Hall effect.

The justification of our choice is based on a calculation by Casimir,⁸ in which it is shown that, for the general case of an anisotropic material, if the vectors are resolved into components in any convenient rectangular coordinate system,

$$E_i = \sum_{j} \rho_{ij} J_j + (\mathbf{r} \times \mathbf{J})_i, \qquad (2)$$

where the ρ_{ij} are functions of **B** such that $\rho_{ij}(\mathbf{B})$ $= \rho_{ij}(-\mathbf{B})$, while $\mathbf{r}(\mathbf{B}) = -\mathbf{r}(-\mathbf{B})$. The vector \mathbf{r} is called the Hall vector. It is seen from Eq. (2) that the Hall field is perpendicular to J.

In the derivation of Eq. (2), Casimir omits the interaction of thermal current and temperature gradient with electric current and potential gradient. Because of this interaction, the Hall effect and magnetoresistive effect depend upon the thermal boundary conditions. A number of experimental investigations have shown that, for metals, when the magnetic field is perpendicular to the elctric current, the electric field component parallel to the current density is not changed by reversing the magnetic field.⁹ This fact has been confirmed on our sample B (20.4°K, 8000 gauss) to within an experimental accuracy of about 0.2 percent. In making these measurements, the magnet was rotated through 360°, taking data every 15°. As a result, we consider that under experimental conditions the Hall field, defined in this way, is perpendicular to the current density, and can be described by a Hall vector in the manner of Eq. (2), without specifying in detail the thermal current or temperature gradient. It is this physical property, which is indicated by both calculation and experiment, that makes our definition seem the most appropriate.

II. EXPERIMENTAL TECHNIQUES

The crystals used in these experiments were grown under vacuum by the Bridgman technique from New Jersey Zinc Company S. P. Zinc.¹⁰ They were 0.030 inch by 0.21 inch in cross section, and from 1 to 2 inches in length. The glass forms used were prepared by shrinking Pyrex glass tubing onto a stainless steel mandrel. Prior to making each form, the mandrel was coated with soot in a candle flame and dipped in a solvent such as CCl₄ to compact the coating. Since the purpose of the soot is to



FIG. 2. Electric circuit. Voltage bd was measured by a Rubicon Type D microvolt potentiometer.

prevent the glass from sticking to the steel, this process was repeated, if necessary, to thoroughly coat the mandrel. The mandrel was then sealed into a length of glass tubing at a reduced pressure and the glass shrunk into the steel by heating in a gas-compressed air flame. When cool, the mandrel usually could be removed easily from the rectangular section.

Prior to use, each crystal was lightly etched and the orientation of the crystal axes determined relative to its geometric shape. Each crystal was mounted in a plastic holder so as to minimize bending of the sample but allow for thermal expansion. To one edge, two potential leads of 0.003-inch copper wire were spot welded. These leads were about 5 mm apart. A third potential lead was welded to the opposite edge, approximately halfway between the other two. Current leads were soldered to the ends of the sample.

The relation of the crystal, Dewar, and magnet is given schematically in Fig. 1. The magnet could be rotated about an axis in the plane of the figure so as to change the direction of the magnetic field. The axis of the Dewar and the current through the crystal were parallel to this axis of rotation. Four-inch pole pieces and a gap of one inch were used. The magnet was calibrated with a search coil and ballistic galvanometer which had been standardized in fields determined by a proton resonance fluxmeter. The magnet calibration was accurate to about 100 gauss. Magnet current was supplied by storage batteries. Both the magnet and control resistors were water-cooled.

The electric circuit is given in Fig. 2. The current through the sample was provided by a storage battery and monitored by an ammeter. For most measurements, this was 3 amp.

Voltages were measured with a Rubicon Type D

⁸ H. B. G. Casimir, Revs. Modern Phys. 17, 343 (1945). ⁹ See, for example, H. B. G. Casimir and A. N. Gerritsen, Physica 8, 1107 (1941); D. Shoenberg, Proc. Cambridge Phil. Soc. ¹⁰ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).



FIG. 3. Laboratory coordinate system.

microvolt potentiometer, using a Leeds and Northrup galvanometer (sensitivity 0.05 μ v/mm at one meter). For convenience an auxiliary lens was used to project the image of the illuminator hairline on a screen. This system provided a magnification of four or five so that galvanometer deflections corresponding to 0.01 μ v could be easily observed.

For crystals A and B, measurements were made to 0.01 μ v. The final measurements on these crystals were reproducible to about this voltage. For crystal C the potentiometer was read to 0.002 μ v because of the smallness of the emf's. After fitting a sinusoidal curve to the data at 77°K for this crystal, the rms deviation of observations from the curve was $6.5 \times 10^{-3} \mu$ v compared with a peak-to-peak amplitude of 0.121 μ v. To obtain this accuracy, it was necessary to insulate the potentiometer battery and the observer.



FIG. 4. Crystal A. r_x as a function of magnet azimuth at 20.4°K.

The noise level in the system varied greatly from experiment to experiment, ranging from about 0.005 μ v to 0.05 μ v. During the last experiments it was discovered that an erratic resistor contact in the magnet control circuit was responsible for the worst of the noise.

The potential difference between any pair of points a, b, c, d could be measured by use of a Leeds and Northrup thermocouple switch enclosed in a sheet metal box. Whatever extraneous voltage this switch introduced caused no trouble, although the switch position was not changed during a series of measurements. For Hall effect measurements, the voltage bd was measured. The other voltages were measured principally when changing samples. In the magnetoresistance measurements referred to earlier, the voltage ac was observed.

The input selector switch of the potentiometer was connected as a reversing switch, so that voltages of either polarity could be measured. Thermal emf's in this switch were less than 0.005 μ v usually.

In principle, only two potential leads on opposite sides of the crystal are necessary in determining the Hall field. By measurements in fields of **B** and $-\mathbf{B}$, the observed voltages can be separated into an ohmic

TABLE I. Hall coefficients at 77°K.

	$R_1 \times 10^{12}$ ohm-cm/gauss	$R_2 imes 10^{12}$ ohm-cm/gauss	
Crystal A	2.5		
Crystal B	1.8	0.21	
Crystal C	0.1	0.19	
Noskov	1.86	0.16	
	2.01	0.19	

potential difference and a Hall voltage. For greatest accuracy, the zero field voltage should be comparable with or less than the Hall voltage. In practice, it is difficult to make such an adjustment of the potential leads. Consequently the circuit of Fig. 2 was used. A copper slide wire S of 60 ohms was connected between potential leads A and C, and the contact adjusted to make the voltage *bd* small in the absence of a magnetic field.

To correct for thermal emf's in the potential leads, voltage *bd* was measured for the same value of current flowing in both senses through the crystal. The voltage due to the current was assumed to be one-half the algebraic difference of the measured values. Results obtained by this analysis were consistent for large variations in the thermal voltages.

Before taking data, the magnet current was usually set at a predetermined value and allowed to stabilize. Only minor adjustments in the control resistors were then necessary. For the most part, measurements were made for magnet orientations spaced at 15° intervals, the magnet being rotated continuously in one direction throughout 360° . Data for magnet settings 180° apart were then combined so as to eliminate thermal emf's and ohmic potential difference.

The ohmic voltage was not analyzed, nor were magnetoresistance data consistently taken.

III. ANALYSIS OF MEASUREMENTS

Kohler has investigated the limitations imposed by crystal symmetry upon the Hall coefficients R_{mn} for the case in which the Hall vector can be written $r_m = \sum_{n} R_{mn} B_n$.¹¹ If, for zinc, we take the 3 direction along the hexagonal axis and the 1 and 2 directions along mutually perpendicular lines in the hexagonal plane, the Hall vector components are

$$r_1 = R_2 B_1, \quad r_2 = R_2 B_2, \quad r_3 = R_1 B_3.$$
 (3)

For analysis of our experimental data, it is convenient to introduce the coordinate system of Fig. 3. The z axis is chosen parallel to the current density. The yz plane is taken parallel to the broad surface of the crystal. It is assumed that the potential contacts on the crystal edges lie in this plane so that the y component of the Hall field is determined by measurement. If the spherical coordinates of the hexagonal axis are α and β , the y component

TABLE II. Coordinates of [0001] and [2110] axes.

	α	β	α'	β'
Crystal A	90°	0°		
Crystal B	32°	-16°	118°	14.5°
Crystal C	8.5°	-40°	95°	0.5°

of the Hall field is

$$F_{y} = -J\{[R_{2}a_{1}^{2} + (R_{2}b_{2}^{2} + R_{1}b_{1}^{2})a_{2}^{2}]B_{x} + [(R_{1} - R_{2})a_{2}^{2}b_{1}b_{2}]B_{y} + [(R_{1} - R_{2})a_{1}a_{2}b_{2}]B_{z}\}, \quad (4)$$

where $a_1 = \cos \alpha$, $a_2 = \sin \alpha$, $b_1 = \cos \beta$, $b_2 = \sin \beta$. If $B_z = 0$, F_y is a sinusoidal function of ϕ , the azimuth of the magnetic field. Knowing values of F_{y} for $\phi = 0^{\circ}$ and $\phi = 90^{\circ}$, it is possible to determine both R_1 and R_2 .

If the Hall field is not linear with magnetic field, the effect can be characterized more directly by giving the Hall vector as a function of ϕ and of the magnetic field strength rather than in terms of field dependent Hall "coefficients." In these experiments, only r_x was determined.

IV. RESULTS

To analyze the data at 77°K, a sinusoidal curve was fitted to the data by the method of least squares¹² and F_y calculated for $\phi = 0^\circ$ and $\phi = 90^\circ$. These values of Hall field were then used to evaluate R_1 and R_2 on the basis of Eq. (4). The results are given in Table I. The extreme values observed by Noskov¹³ are also indicated.



FIG. 5. Crystal A. r_x as a function of magnet azimuth at 8200 gauss.

Measured values of α and β are listed in Table II. Similar spherical coordinates, α' and β' , for the [2110] axis are also tabulated.

For crystal C, the calculation of R_1 was strongly dependent upon $F_y(\phi=90^\circ)$. If the value used were in error by a factor of -20, the value of R_1 would be about 2×10^{-12} ohm-cm/gauss. Such a change in $F_y(\phi=90^\circ)$ would decrease R_2 to 0.17×10^{-12} ohm-cm/gauss. It is not unreasonable that $F_y(\phi=90^\circ)$ might be in error by so large a factor. Assuming values of 2×10^{-12} and 0.2



FIG. 6. Crystal C. r_x as a function of magnet azimuth at 20.4°K.



FIG. 7. Crystal C. r_x as a function of magnetic field strength $= -22^{\circ}$, 20.4°K. The points at 8200 gauss and 10,200 gauss are from the rotation diagrams of Fig. 6.

¹¹ M. Kohler, Ann. Physik 20, 878 (1934).

¹² This procedure was adopted for convenience. We do not otherwise justify its use. ¹³ M. M. Noskov, J. Exptl. Theoret. Phys. (U.S.S.R.) 8, 717

^{(1938).}



FIG. 8. Crystal A. Voltage bd as a function of magnetic field strength. $\phi = 0^{\circ}$.

 $\times 10^{-2}$ ohm-cm/gauss for the Hall coefficients, the Hall potential difference across the thickness of this crystal for $\phi = 90^{\circ}$ can be estimated as about thirty times the potential difference across the width of the crystal. Accordingly, the discrepancy in this value of R_1 can be explained by assuming that the potential contacts did not lie in the yz plane.

Values of r_x at liquid hydrogen temperatures are given in Figs. 4 through 7. For crystal A, the data at 20.4°K are symmetric about $\phi = 0^{\circ}$. The curve at 14°K has been drawn accordingly.

For crystal B, plots of r_x vs ϕ at 20.4°K, 8200 and 10,200 gauss, are nonsinusoidal and somewhat skewed. They do not exhibit as pronounced a variation with field as those for either crystal A or C. Data taken at 14°K indicate a pronounced temperature dependence. Because of poor temperature control, these data were not sufficiently reproducible to be quantitatively significant.

Of the rotation data on crystal C little can be said other than that the Hall vector is nonlinear with magnetic field. The reproducibility of the data is indicated by the sets of points at 83°. In Fig. 7, the points at 8200 and 10,200 gauss were taken from the rotation data of Fig. 6.

A set of measurements were made on crystal A for $\phi = 0^{\circ}$, $T = 20.4^{\circ}$ K, to look for a relationship between the Hall effect and de Haas-van Alphen effect, i.e., the field dependence of magnetic susceptibility.^{1,2} The observed voltages, corrected for thermal emf's, are plotted in Fig. 8. Since corresponding measurements were not made at $\phi = 180^{\circ}$, it is not possible to separate the observed voltage into ohmic potential and Hall emf. From Fig. 4 the ohmic potential can be estimated as about 5 percent of the observed voltage. The results of Lazarev, Nakhimovich, and Parfenova³ for a crystal of similar

orientation indicate that $\Delta R/R_{H=0}$ increases nearly linearly with magnetic field by about 14 percent per kilogauss. As a consequence, it is unlikely that there are any oscillations in r_x for this orientation of crystal A in excess of 2 percent of r_x .

For comparison, corresponding measurements are given for 77° K. For a fixed field strength, the difference in voltage between these two sets of data is almost exactly equal to the ohmic potential difference in the measurements at 77° K.

Lazarev, Nakhimovich, and Parfenova^{8,4} have reported magnetoresistance measurements on a single crystal of zinc for which, in terms of our coordinate system, $\alpha = 88^{\circ}$, $\beta = 0^{\circ}$. The magnetic field was in the xy plane. At 4.2°K, they observed an anomaly in the resistance for fields between 8000 and 10,000 gauss at $\phi = 0^{\circ}$. For $\phi = 5^{\circ}$, the anomaly was no longer observed, nor was it evident at 20.4°K, $\phi = 0^{\circ}$. Since crystals of several orientations were examined in their experiments and no further anomaly reported, the inference is that no other anomaly was evident in the data.

Gerritsen and de Haas,⁶ and Gerritsen, de Haas, and van der Star⁷ have studied the Hall effect in bismuth crystals and observed a qualitative correlation with the de Haas-van Alphen effect. No such correlation is apparent for the case of zinc. On the contrary, with the magnetic field parallel to the hexagonal axis, the Hall vector seems to be linear with magnetic field, whereas the susceptibility oscillates. When the magnetic field is perpendicular to the hexagonal axis, the susceptibility is not strongly dependent on magnetic field, while the Hall vector is nonlinear.

During this research Borovik¹⁴ reported measurements on Hall effect on one zinc crystal for $\phi = 0^{\circ}$ and various field strengths. Since his sample was of different crystallographic orientation than any of ours, no direct comparison is possible. There does not seem to be any discrepancy between his results and ours.

In summary, these experiments show that at 20°K, the Hall effect is of the same order of magnitude as at 77°K. While the Hall vector for the latter case is a linear vector function of magnetic field, for the former it is not. The nature of this nonlinearity depends upon the crystallographic orientation of the magnetic field. Finally, no relationship was observed between Hall effect and either magnetoresistance or de Haas-van Alphen effect. Further experiments are planned in which a more systematic investigation will be made of both Hall effect and magnetoresistance.

¹⁴ E. S. Borovik, Doklady Akad. Nauk S.S.S.R. 70, 601 (1950).