# ON THE HALL EFFECT AND ELECTRICAL RESISTIVITY OF Zn SINGLE CRYSTALS

by

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Abstract. Hall effect and resistivity measurements were conducted on a number of single crystals of Zn.

The temperature dependence of 4 single crystals resistivity was examined, and found to obey a linear relationship in accordance with Case and Gueths predictions.

It has been shown |1| that for anisotropic metals one could write for the galvanomaguetic effects:

$$E_{i} = \rho_{ik}j_{k} + (\overrightarrow{A} \times \overrightarrow{J})_{i} \tag{1}$$

where  $E_i$  are the components of the electric field  $\rho_{ik}$  the resistivity tensor

jk the components of the current's density

A the Hall vector defined as an odd function in B i.e.

$$\vec{A}(\vec{B}) = -\vec{A}(-\vec{B})$$

where all the components refer to a suitable rectangular coordinate system.

If the effect of microscopic reversibility and crystal's symmetry are taken into account it has been proved |2, 3, 4| that from the 27 existing components of the Hall tensor only two are independent, designated  $R_H$  and  $R_I$  according to the magnetic's field direction, the same applying to the resistivity tensor components as well.

Hall effect measurements on Zn single crystals have been reported earlier [5, 6, 7] and are tabulated in Table II.

Noskov's | 5 | results were met with some caution | 8 | for several

 $TABLE\ I$  Hall and resistivity components of Zn single crystals

|         | Orientation* |      | Phase* | $\mathrm{R}_{ff} 	imes 10^{10}$ | $R_1 \times 10^{10}$ | $\rho \times 10^8$ | $\rho_{II} \times 10^8$ | $\rho_1 \times 10^8$ |
|---------|--------------|------|--------|---------------------------------|----------------------|--------------------|-------------------------|----------------------|
| $N^{0}$ | ε            | δ    | shift  | $(m^3/A.s)$                     | $(m^3/A.s)$          | $(\Omega.m)$       | $(\Omega, \mathbf{m})$  | $(\Omega.m)$         |
| 1       | 49           | 104  | 47.60  | 1.58                            | -0.23                | 5.981              |                         |                      |
| 2       | 39           | 44   | 54.80  | 1.40                            | -0.26                | 6.001              |                         |                      |
| 3       | 74           | 46   | 14.50  | 1.36                            | -0.31                | 5.982              |                         |                      |
| 1/k     | 40           | -19  | -27.00 | 1.29                            | -0.14                | 6.016              | $6.05 \pm 0.12$         | $5.98 \pm 0.14$      |
| 5       | 68           | 43   | 18.30  | 1.37                            | -0.23                | 5.985              |                         |                      |
| 6       | 52           | 71   | 47.53  | 1.39                            | -0.35                | 5.982              |                         |                      |
| 7       | 35           | 63   | 64.00  | 1.46                            | -0.20                | 5.990              |                         |                      |
| 8       | 26           | -96  | -79.00 | 1.38                            | -0.18                | 5.980              |                         |                      |
| 9       | 64           | 31   | 16.00  | 1.60                            | -0.18                | 5.990              |                         |                      |
| 10      | 72           | -105 | -22.00 | 1.41                            | -0.36                | 5.980              |                         |                      |
| 11      | 65           | 108  | 29.40  | 1.41                            | -0.19                | 5.981              |                         |                      |

<sup>\*</sup> in degrees

TABLE II

Hall effect measurements on Zn single crystals

| No | $R_{,,}(10^{-10}\frac{m^3}{Cb})$ | $R_{i}(10^{-10}  \frac{m^{3}}{Cb})$ | Author(s)   |
|----|----------------------------------|-------------------------------------|-------------|
| 1  | 1.44                             | -0.04                               |             |
| 2  | 1.41                             | _                                   |             |
| 3  | 1.43                             | 0                                   | Noskov      |
| 4  | 1.43                             | -0.06                               | (288° K)    |
| 5  | 1.44                             | -0.025                              |             |
| 6  | 1.4                              | _                                   |             |
| 1  | 2.5                              | _                                   |             |
| 2  | 1.8                              | -0.21                               | Logan       |
| 3  | 0.1                              | _                                   | (77° K)     |
| 1  | 1.4                              | -0.14                               |             |
| 2  | 1.7                              | -0.32                               |             |
| 2  | 1.4                              | -0.32                               |             |
| 3  | 1.8                              | -0.33                               | Lane-Huglin |
| 4  | 1.6                              | -0.30                               | - Striuger  |
| 5  | 1.4                              | -0.26                               | (297° K)    |
| 6  | 2.5                              | -0.23                               |             |
| 7  | 1.9                              | -0.14                               |             |
| 8  | 1.4                              |                                     |             |

reasons. First of all it was felt that the number of crystals employed (6) was unadequate, since the softness of several crystals would make them bend under their own weight if held at one end producing strains in the crystals. It has been proved that deliberately deformed crystals

would give a 10% difference in the Hall effect value of the underformed state.

The main point of critism was concerned though, with the way Noskov obtained the values of  $R_H$  and  $R_I$ .

In cases where  $R_{II}$  was a rapidly varying function of the crystal-lographic orientation, i.e. angles  $\varepsilon$ ,  $\delta$ , the angles were adjusted to give agreement for the larger componed  $R_{II}$  the value of which was obtained directly from a crystal posessing faronrable orientation,  $R_{II}$  then being calculated from those adjusted values.

Since the value of  $R_{//}$  could be different for different reasons in two crystals (i.e. strain, substructure, impurity levels etc.) this method doesn't seem to be justified.

More careful determination was conducted by Lane Huglin and Stringer [7]. Some sceptisism is involved in their work as well, concerning the rather visual estimation of the phase angle  $\psi$ , though they quote a detailed examination of the «angular errors» involved. It is also worthnoting that crystals possesing the same orientation (i.e. labeled 3, 4 in their work) are assigned different  $R_H$  and  $R_I$  values, which implies that either an error is involved or some other causes such as those quoted above prevail.

As far as resistivity measurements are concerned there seems to be nothing new to the data quoted by Meaden | 9 | and Hurd | 1 |. Determination of resistivity on polycrystals by Kuvandikov — Cheremushkina | 10 | as a function of temperature does not seem to add any useful information to the so far existing.

#### EXPERIMENTAL PROCEDURE AND RESULTS

As starting material for the preparation of the single crystals, Zn rods of 5N nominal purity were used, supplied by Koch Light Laboratories.

The method adopted for growing single crystals was a modified Bridgmann technique described elsewhere |11|. The as grown specimens, of rectangular shape and dimensions  $10 \times 0.45 \times 0.5$  cm³ were cut to required dimensions of approximately  $3 \times 0.45 \times 0.5$  cm³ by using and acid saw and etching them afterwards.

The orientation determination was effected by a conventional back reflection Laue technique.

All specimen showing appreciable asterism were rejected. The Laue technique was used as an additional check of the homogeneity of the crystals.

The Hall effect was measured using the method developed by Stringer and coworkers | 7, 12, 13, 14 | in which the Hall signal is determined as a function of the angle  $\Theta$ , which is the angle between the magnetic induction lying in the plane normal to the current direction, and the normal to the current direction. The sine curve resulting from a plot of Hall voltage versus  $\Theta$  is effectively displaced by an angle  $\psi$  due to different contributions to the Hall signal from  $R_H$  and  $R_I$  as the hexad axis is rotated relative to the magnetic field.

The  $R_H$  and  $R_I$  can be calculated from the Hall peak voltage and the displacement  $\psi$ , using equations |7|:

$$R_{II} = R\left(\frac{\pi}{2}\right) + R(0) \frac{\cot \varepsilon}{\sin \delta}$$

$$R_1 = R\left(\frac{\pi}{2}\right) - R(0) \frac{\tan \varepsilon}{\sin \delta}$$

where

$$R\left(\frac{\pi}{2}\right) = \frac{V_H t}{BI} = R_{max} cos \psi$$

$$R(0) = \frac{V_H t}{BI} = R_{\text{max}} \cdot \sin\!\psi \ .$$

The Hall peak voltage  $V_{max}$  and the phase angle  $\psi$  are determined by a computer program developed | 11 |. Errors involved in computing the Hall components arise mainly from errors in determining  $\epsilon$ ,  $\delta$ ,  $\psi$  as well as in determining the specimen's thickness.

The last errors shouldn't be more than 1%, the thickness of the specimen being determined by a traveling microscope. Following Lane |7| the dependence of  $R_{II}$  and  $R_{I}$  values on «angular» errors  $\epsilon$ ,  $\delta$  are plotted in Fig. |1-10|.

Although it is not probable that an error larger than  $\pm 1^{\circ}$  was involved, we have scanned a bandwidth of  $10^{\circ}$  both sides of the calculated value.

It is evident that for several crystals possessing particular orientations the  $R_{//}$  and  $R_1$  critically depend on the angular errors. For instance in crystal No 3 variation of  $\epsilon$  by 1° alters the value of  $R_1$  from

-0.31 to -0.42 ( $10^{-10}$  m<sup>3</sup>/Cb) which is over 20%. It would be therefore suggested that the values of crystals 3,5,9,10 are most sensitive to angular errors.

As far as heat treatment was concerned all specimens examined, showed the same behaviour i. e. the Hall signal increasing after heat treatment of 24 hours at 150° C to reach a steady value after 48 hours. The specimens were therefore annealed for 72 hours at 150° C degrees hefore taking a Hall measurement.

Resistivity measurements were conducted alongside with Hall effect measurements on the same specimens. A four probe d-c. conventional method was used throughout, using a current of 0.1 Amp. provided by a Tinsley stabilizer with nominal stability of 1 ppm. As an additional check the current was monitored through a 0.1  $\Omega$  standard resistor by measuring the potential drop using an additional potentiometer. This proved to be quite unnessecary the stability of the current being realy as claimed.

The resistivity components  $\rho_{IJ}$  and  $\rho_{I}$  was eliminated by using the equation:

$$\rho = \rho_{1/\cos^2 \epsilon \cos^2 \delta} + (1 - \cos^2 \epsilon \cos^2 \delta) \rho_1.$$

Knowing  $\rho$  for a given temperature, for two at least crystals of different orientations, a set of simultaneous equations results which enables determination of  $\rho_{//}$  and  $\rho_1$ . Having measured resistivity on all of the crystals presented here, a large number of combinations resulted, consistently giving the values of  $\rho_{//}$  and  $\rho_1$ .

Resistivity measurements as a function of temperature, were conducted by using a temperature controlled silicone bath, contained in a dewar flask, on four single crystals. Temperature control proved to be quite critical on the stability of the signal detected.

Since the temperature stability was not hetter than  $\pm$  0.5° C no attempt was made to eliminate  $\rho_{ff}$  and  $\rho_{f}$  for temperatures different than room temperature, though it would be very helpful since the behaviour of the anisotropy ratio  $a=\rho_{ff}/\rho_{f}$  as a function of temperature could be deducted.

The measurements at each temperature were conducted for both directions of the primary current.

#### DISCUSSION

Several models have been proposed so far in the effort to explain the behaviour of galvanomagnetic phenomena in hcp metals. The proposed models are mainly based on our knowedge of the Fermi surfaces of the metals involved, as they result from other experimental methods (i. e. de Haas van Alphen effect magnetoresistance measurements etc.) using several assumptions or simplifications leading to analytical computation of the galvanomagnetic tensor components.

Those models vary from oversimplified ones, to very complex indeed. For instance the simple picture of the hole states in Cadmium according to Stringer-Hill and Huglin |43| are simply cylinders with the long axis along  $x_3$  direction giving no Hall effect when the magnetic field is applied along any direction in  $x_1x_2$  plane.

As a first effort to predict the experimental data from a more detailed analysis of the Fermi surface the method followed by Tsuji and Kunimune should be considered. They used |15| a simplified Fermi surface for Cd along with the basic ideas of the two band model.

In their calculations the hole states are represented by three elliptical toroids of elliptical cross section.

The electron surface is assumed having the shape of an ellipsoid of revolution. Proper effective masses are assigned to both states. The Boltzmann equation is then solved for both bands and the components of the galvanomagnetic tensor calculated.

Although the model was effective in predicting the right order of magnitude for the Hall effect it couldn't account for the magnetoresistance and vice versa.

Cowley | 16,17 | commended that the reason might be in their choice of the Fermi surface which is very far from the real Fermi surface.

A more detailed and general approach was made by Cowley and Stringer [16,17]. Using the planar faced energy surface (PFES) method introduced by Allgaier [48,19] they tried to explain Hall effect in hcp metals and alloys with moderate success. In their approach the Fermi surface is approximated by simple geometrical shapes (polygons) and only the second and third zones are taken into account. They were able to postulate almost exact values of the Hall effect components in Cd and Zn, though they couldn't sufficiently account for the difference in sign appearing in Zn.

According to our experimental results the two Hall coefficients in Zn have a «best value» of 4.39 and -0.28 (40<sup>-10</sup> m³/Cb) correspondingly which is in good agreement with the values found by Stringer group, and are shown in Table I. It is also known that the Fermi surfaces of both Zn and Cd are quite similar and there shouldn't be any reason why the Hall components in these metals should vary that much.

In trying to account for this occurence the previous workers tried several methods. They adjusted the shape of the monster for Cd as much as 10% expecting to increase the contribution to  $R_{II}$  which was not found to be the case. They succeeded in doing so only when they weighted the contributions of the two Fermi sheets differently by allowing the velocity of the lens to be 20% lower than the velocity of the monster.

The major drawback of this model is the large number of assumptions used as far as the shape of the surface and shape of the monster used are concerned, as well as the assumed carriers velocities, lens aspect ratio etc.

Lately another effort has been made by Shiozaki | 20 | to calculate the Hall effect in the low field region of both Cd and Zn.

The main aim of this work was to eliminate as many arbitrary assumptions as possible and to exactly calculate as many contributions as possible from various parts of the Fermi surface to Hall effect components.

She calculated the contributions from six different parts of the Fermi surface separately i. e. the contributions from monster, lens, needles, butterflies and cigars which means from the four zones separately.

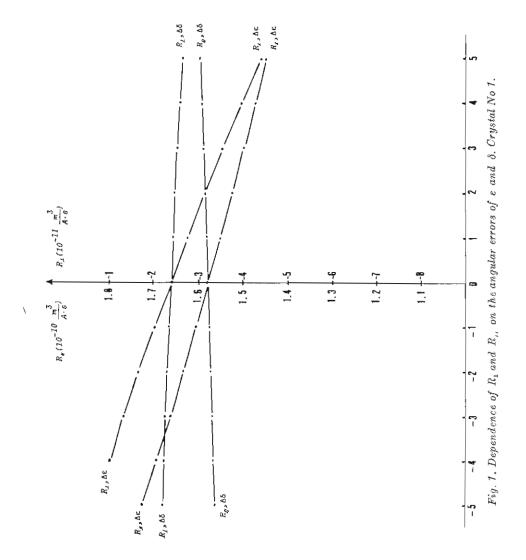
The Hall coefficients are obtained by means of the formulae established in a previous paper for Be | 21 |.

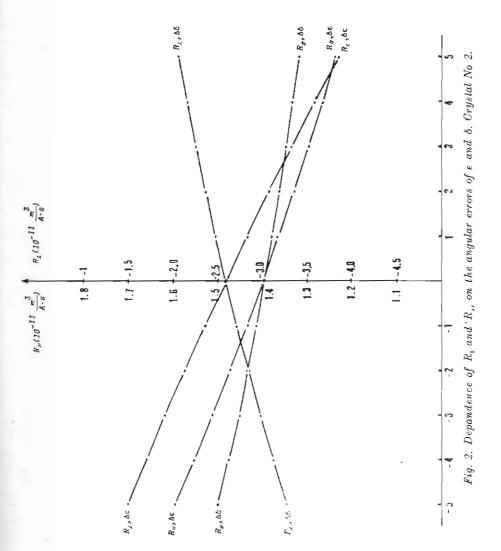
$$R = -\frac{\Sigma^{1}_{xyz} + \Sigma^{2}_{xyz} + \Sigma^{2}_{xyz} + \Sigma^{4}_{xyz} + \Sigma^{5}_{xyz} + \Sigma^{6}_{xyz}}{(\sigma^{1}_{xx} + \sigma^{2}_{xx} + \sigma^{3}_{xx} + \sigma^{4}_{xx} + \sigma^{5}_{xx} + \sigma^{6}_{xx})^{2}}$$

$$R = -\frac{\Sigma^{1}_{yzx} + \Sigma^{2}_{yzx} + \Sigma^{3}_{yzx} + \Sigma^{4}_{yzx} + \Sigma^{6}_{yzx} + \Sigma^{6}_{yzx}}{(\sigma^{1}_{xx} + \dots + \sigma^{6}_{xx})(\sigma^{1}_{zz} + \dots + \sigma^{8}_{xx})}$$

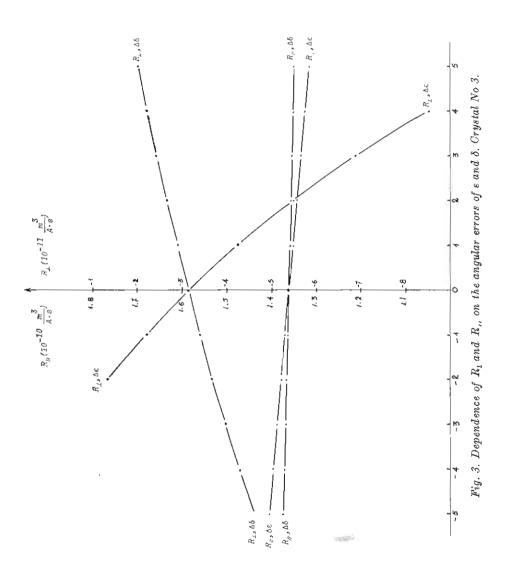
Where superscripts correspond to various parts of the Fermi surface and namely 1 for caps to 6 for cigars in the order referred above. The model predicts nicely the experimental data for both metals at 77° K with no allowance though for temperature dependent contributions.

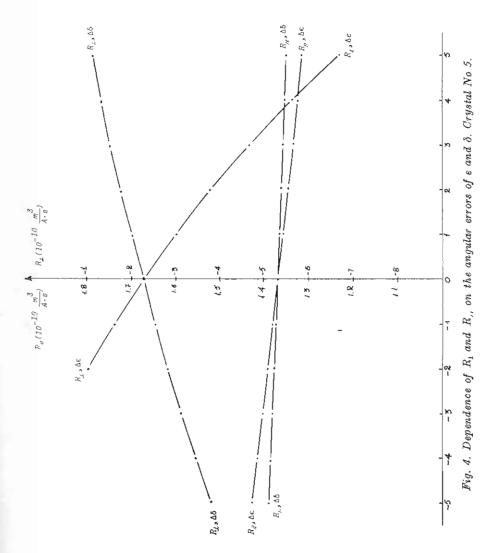
As far as resistivity measurements are concerned, our room temperature resistivities compare quite favourably with values quoted by Meaden |9| and Hurd |1|. The temperature depedence of the four single crystals examined which is linear, is idendical with the temperature dependence found in sereval polycrystals by Cheremushkina and Kuvandnikov |10| and is shown in Fig. |11-14|. It is worthnoting that



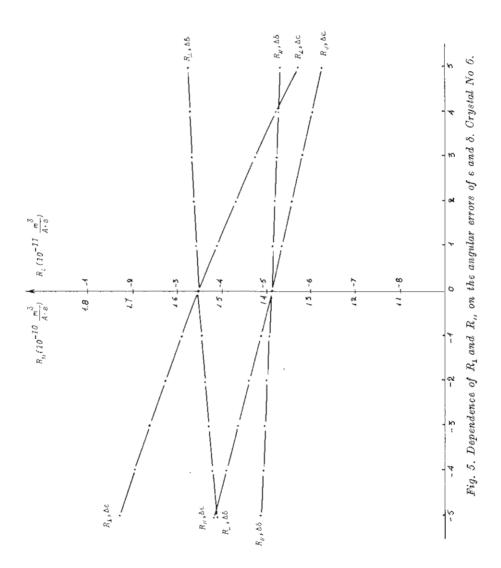


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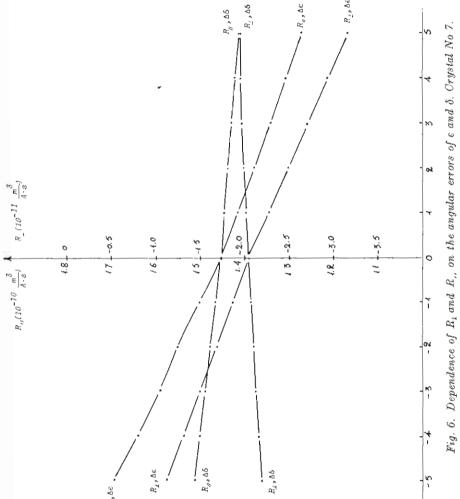


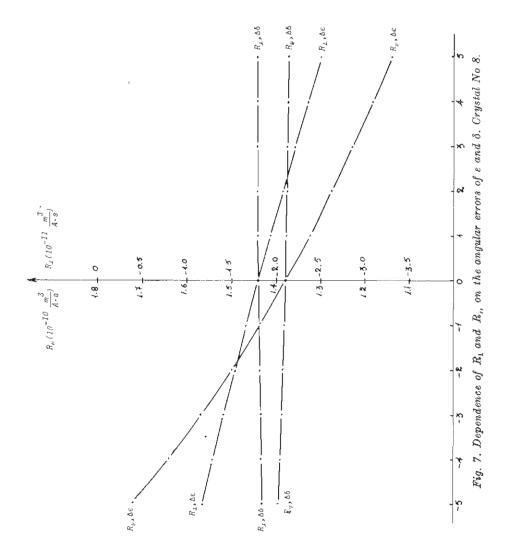


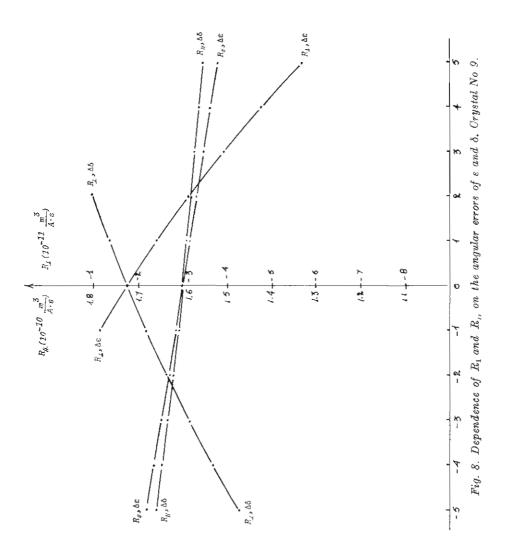
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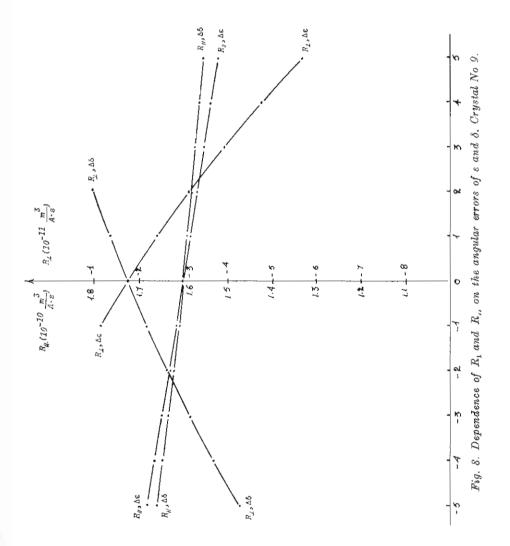


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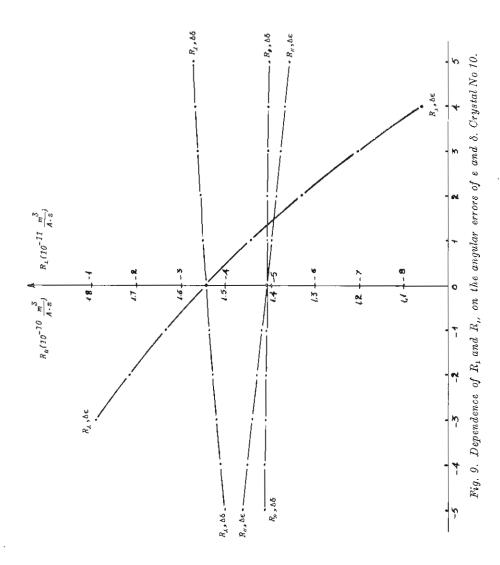




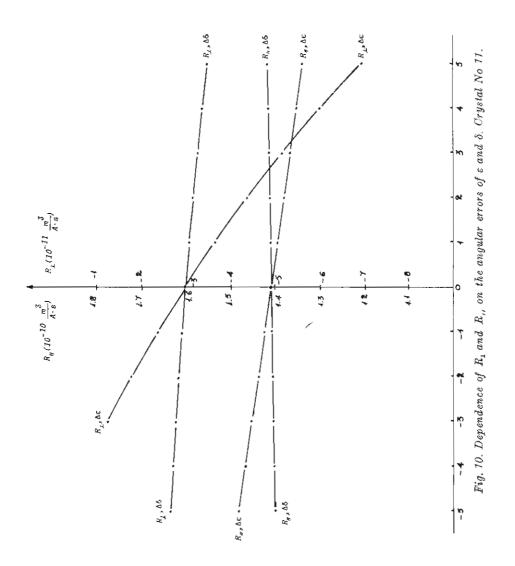




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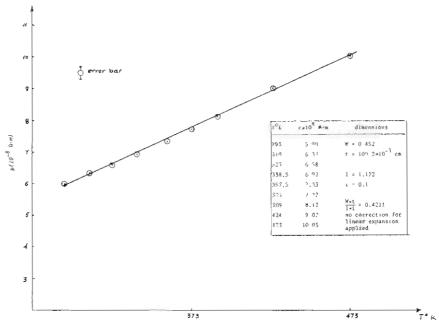


Fig. 11. Temperature dependence of the resistivity in Zn. Crystal No 4.

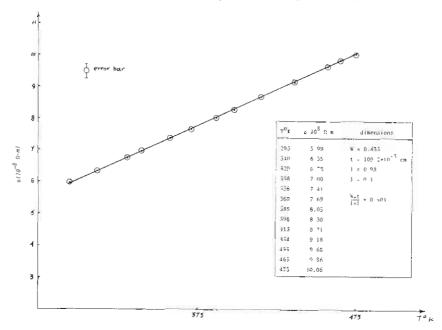


Fig. 12. Temperature dependence of the resistivity in Zn. Crystal No 7.

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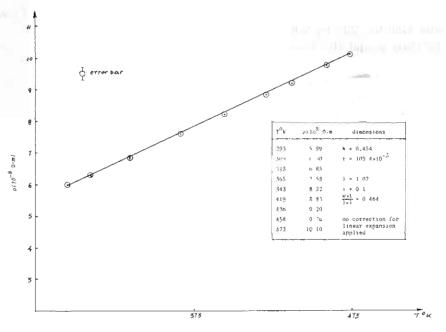


Fig. 13. Temperature dependence of the resistivity in Zn. Crystal No 9.

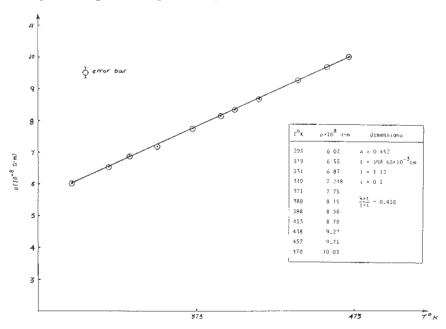


Fig. 14. Temperature dependence of the resistivity in Zn. Crystal No 10.

this linear dependence is predicted by the model put forward by Case and Gueths |22| by which they tried to explain their results in  $\beta$ -Sn. In their model the Fermi surface of the hexagonal metals are not far removed from a sphere.

They assumed that in certain directions the sphere is extending beyond the Brillouin zone. These parts are taken to be of spherical curvature and to completely dominate the conductivity in the directions subtended by them.

In the high temperature region they find that if an isotropic relaxation time is prevailing the resistivity is linear in temperature which is found to be true in our case.

#### REFERENCES

- 1. HURD C. Adv. Physics 23, 315 (1974).
- De Groot, S. R. Thermodynamics of Irreversible Processes (Amsterdam North Holland 1951).
- 3. SMITH A. C. JANAK J. F. Electronic Conduction in Solids. and ADLER R.B. Electronic Conduction in Solids (McGraw Hill N. Y. 1967).
- 4. CASIMIR H. B. G. Rev. Modern Phys. 17, 343 (1945).
- 5. Noskov N. M. Zh. Eksperim i Teor Fiz 8, 717 (1938).
- 6. Logan J. K. Markus J. A. Phys. Rev. 88, 1234 (1952).
- 7. Lane. S Huglin A. S. Stringer J. Phys. Rev. 135, 1060 (1964).
- HILL J. "Hall effect in Cd-Mg Cd-Hg alloys" Ph. D. Thesis Univ. of Lpool (1969).
- 9. Meaden G. T. Electrical Resistance of Metals (N. Y. Plenum 1965).
- Kuvandikov O. K. Cheremushkina A. V. Vasil'eva R. P. Fiz. Met. Metall. 34 867 (1972) (Engl. transl. in Phys. Met. Metall (GB)).
- A. TSOUKALAS H. PAPADIMITRAKI-CHLICHLIA Hall effect and resistivity in Cd (In Press).
- 12. ALTY J. L. STRINGER J. Phys. Stat. Sol. 32, 243 (1969).
- STRINGER J. HILL J. HUGLIN A. S. Phil. Mag. 21, 53 (1970). Phys. Stat. Sol. (a) 13, 67 (1972).
- 14. STRINGER J. HILL J. HUGLIN A. S. Phil. Mag. 29, 869 (1974).
- 15. TSUJI M. KUNIMUNE M. J. Phys. Soc. Japan 18, 1569 (1963).
- 16. COWLEY P. H. STRINGER J. Phil. Mag. 29, 99 (1974).
- 17. COWLEY P. H. STRINGER J. Phys. Rev. B8, 2519 (1973).
- 18. Aligaier R. S. Phys. Rev. 158,699 (1967).
- 19. Allgaier R. S. Phys. Rev. 165, 775 (1968).
- SHIOZAKI I. J. Phys. F. 6, 1523 (1976).
- Shiozaki I. J. Phys. F. 5, 451 (1975).
- 22. Case S. K. Gueths J. E. Phys. Rev. B2, 3843 (1970).

#### ΠΕΡΙΛΉΨΤΣ

## ΠΕΡΙ ΤΟΥ ΦΑΙΝΟΜΈΝΟΥ HALL ΚΑΙ ΤΗΣ ΕΙΔΙΚΉΣ ΗΛΕΚΤΡΙΚΉΣ ΑΝΤΙΣΤΑΣΕΩΣ ΜΟΝΟΚΡΥΣΤΑΛΛΩΝ Zn.

#### όπΥ'

### ΙΩΑΝΝΟΥ Α. ΤΣΟΥΚΑΛΑ - Ε. ΠΑΠΑΔΗΜΗΤΡΑΚΗ - ΧΛΙΧΛΙΑ

Εἰς τὴν παρούσαν ἐργασίαν μελετᾶται τὸ φαινόμενον ΗαΙΙ καὶ ἡ εἰδικὴ ἡλεκτρικὴ ἀντίστασις μονοκρυστάλλων ψευδαργύρου.

Διὰ τὸ φαινόμενον Hall εὑρέθησαν συντελεσταὶ  $R_{II}=1.39,\ R_1=-0.28$  ( $10^{-10}\ m^3/{\rm Cb}$ ) ἐν καλῆ συμφωνία μὲ τὰς μέχρι σήμερον γνωστὰς τιμάς.

Αἱ ἀντίστοιχοι τιμαὶ τῶν συνιστωσῶν τῆς εἰδικῆς ἠλεκτρικῆς ἀντιστάσεως εὑρέθησαν  $\rho_H=6.05$  καὶ  $\rho_{\rm I}=5.98$  ( $10^{-10}$   $\Omega$ .m). Ἡ ἐξάρτησις τῆς εἰδικῆς ἠλεκτρικῆς ἀντιστάσεως ἐκ τῆς θερμοκρασίας διὰ τέσσαρα μονοκρυστάλλους εὑρέθη νὰ ἀκολουθῆ γραμμικὴν σχέσιν, ὡς προβλέπεται ὑπὸ τῶν Case-Gueths.