Investigation of Hall Resistivity and Magnetoresistance of Cadmium and Cadmium-Zinc Crystals*

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Measurements of the Hall resistivity and magnetoresistance of cadmium and cadmium-zinc crystals in the residual-resistance-ratio range of 40 000–240, corresponding to a maximum zinc concentration of 1.5 at. %, are reported in the temperature ranges of 1.4–4.2, 9–20, and at 77 K for magnetic fields below 25 kG. The Hall resistivity is positive for values $\omega\tau<1$, but below 20 K and for $\omega\tau>1$ it can be positive or negative, depending on temperature and impurity concentration. The results indicate that the concept of a single static electron scattering time has to be abandoned in the case of reduced phonon scattering. The similarity between the effects of impurity and pressure on the Hall resistivity is indicated to be compatible with the concept of intersheet scattering.

I. INTRODUCTION

THE Hall resistivity of cadmium is known[1–3] to be positive between 14 and 300 K. In recent studies of size-dependent oscillatory effects in pure cadmium crystals, it was found[4,5] that the magnitude of the Hall resistivity becomes negative below 4 K. Discarding the oscillatory effects, the magnitudes of the observed Hall resistivities and their field dependence in general do not agree, even though the purity of the crystals is roughly of the same order. Neither a systematic investigation nor a general explanation for the differences and the observed sign reversal at low temperatures has been published yet. Also, the magnetoresistance deviates from the normal pattern. The reduced Kohler diagram[6] exhibits a quadratic magnetoresistance for large $\omega\tau$ and less than quadratic for small $\omega\tau$ values.

Perusal of the published data suggests that the Hall resistivity is very sensitive to sample contamination and that the observed differences may have their origin in small differences in the amount and kind of impurities. The data suggest further that the effect of such impurities cannot easily be accounted for by the normal concept of a temperature-independent impurity scattering. It cannot be concluded from the available data whether the observed effects are the consequence of particular deviations from the general concept of temperature-independent impurity scattering or whether a more interesting phenomenon connected with the electron scattering time is involved.

For these reasons, a systematic experimental investigation of the effect of impurities and temperature on the Hall resistivity and the magnetoresistance of cadmium has been started. Zinc was chosen as an impurity. Not only does Zn in Cd presumably leave the electron/atom ratio (e/a) unchanged, but it has proved to be a technically favorable element for the preparation of the dilute alloy crystals starting with a pure crystal.

II. EXPERIMENTAL METHOD

Single-crystal samples of Cd and Cd-Zn were prepared from a commercially obtained cylindrical cadmium single crystal of reasonable purity[7] (2.5 cm in diam and 10 cm in length). Samples were cut from this source and planed with a spark cutter (SMC Servomet). The piece from which the sample slices were cut was oriented by x-ray diffractometry to better than 1°. The deteriorated layer caused by the spark cutter was removed by reduction of the sample dimensions by at least 0.2 mm in a solution of dilute nitric acid and ethanol. The alloys were obtained by the diffusion of electroplated Zn into such pieces of the pure crystal. For the electroplating, a solution of $ZnCl_2$(220 g/liter) and NH_4Cl(268 g/liter) in water proved to be reliable.[8] Good deposits were obtained in 10–15 min with a dc current of 15–20 mA/cm², using two zinc anodes (purity 99.999%) and the sample as the center cathode. The temperature of the bath was kept within 50–60 C. These electroplated samples were heated at 200 C in helium atmosphere for 1 to 8 days, depending on a rough estimate of the Zn concentration needed. The plating was then etched off and the samples were homogenized at 200 C for a number of days, so that the total time of the samples at 200 C was 12 days. After this process the homogeneity of the samples proved to be rather good. The drop in resistance from room temperature to 4.2 K of a test sample made in such a manner changed from 467 to 500 when the thickness of the sample was reduced

* Work supported in part by the National Science Foundation, the Purdue Research Foundation, and the Advanced Research Projects Agency.
† This work is part of the requirement for a Ph.D. degree.
[1] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1965), 2nd ed., Chap. 8, p. 214.
[2] R. Jaggi, in *Landolt-Bornstein*, edited by R. Bechmann *et al.* (Springer-Verlag, Berlin, 1959), Vol. II, Part 6, p. 161.
[3] G. S. Lane, A. S. Huglin, and J. Stringer, Phys. Rev. 135, A1060 (1964).
[4] C. G. Greiner, K. R. Efferson, and J. M. Reynold, Phys. Rev. 143, 406 (1966).
[5] H. J. Mackey, J. R. Sybert, and J. T. Fielder, Phys. Rev. 157, 578 (1967).
[6] A. N. Gerritsen, in *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 137.
[7] The cylindrical bar of cadmium was obtained from Harshaw Chemical Company.
[8] E. J. Smith, in *Modern Electroplating*, edited by Frederick A. Lowenheim (John Wiley & Sons, Inc., New York, 1963), 2nd ed., p. 396.

from 1.0 mm to 0.5 mm. The Cd-Sn sample was obtained by coating a piece of cadmium crystal with molten tin using a clean solder iron. The resistance drop of a test piece of a Cd-Sn alloy changed from 3350 to 3475 when the thickness was reduced to half of the original thickness. X-ray diffraction checks for some of the alloys with Zn and the Cd-Sn alloy did not show observable deviations from the pure single crystal. A test piece of pure cadmium was also heated at 200 C in helium atmosphere for 12 days. The observed resistance drop to 4.2 K did not differ within the experimental error from that for the untreated sample. Finally, the samples were cut in the shape shown in Fig. 1. In addition to a number of alloy samples prepared in the manner described, one sample with a resistance ratio $r=R_{273}/R_{1.4}=6917$ (R_T is the sample resistance at temperature T) was cut from a commercially made Cd-Zn alloy.[9]

In order to keep the samples available for further investigation, only two samples, having $r=240$ and $r=427$, were subjected to mass spectroscopic analysis, which indicated that Zn was present in the amounts of 1.5 at.% and 0.56 at.%, respectively, and that no other impurities were introduced during the preparation of the samples.

For the measurements of transverse magnetoresistance and Hall resistivity the samples were mounted so that the electric current was along [10$\bar{1}$0] and the magnetic field along [0001]. Potential leads were soldered with thermal-free solder (Leads and Northup) on the arms of the sample as shown in Fig. 1. A conventional cryostat in which the sample was in contact with the bath was used for the temperatures ranges 1.4–4.2, 9–20, and at 77 K. A regulated power supply (Lambda LA50-03B) delivered dc currents up to 1.5 A. Observation of the rotation diagram at 4.2 K made the adjustment of $H\|[0001]$ possible within 1°. Magnetoresistances were measured with a five-digit Diesselhorst Compensator (Bleeker) in combination with a 10^{-4}-Ω standard resistor (Otto Wolff Berlin) and a galvanometer (Kipp, type Zc). Hall voltages, resistances $<10^{-7}$ Ω, and the angular dependence of the magnetoresistance were measured with a dc microvolt amplifier (Guildline, sensitivity 10^{-9} V) in combination with an X-Y recorder. The Hall voltages were measured in the usual manner with successive reversals of current and field so that the various components of each potential, odd and even in current and field, could be separated.

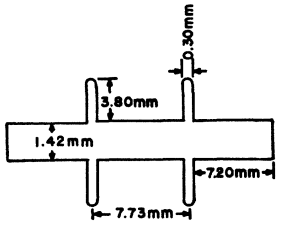

FIG. 1. Geometry and dimensions of the 1.13-mm-thick Cd sample ($r=40\,000$). The axis of the sample is [10$\bar{1}$0], and [0001] is perpendicular to the plane of the sample.

[9] The Cd-Zn crystal was obtained from Aremco Products, Inc.

III. EXPERIMENTAL RESULTS

For later comparison the resistance (R)-versus-temperature curves of the samples below 20 K are of interest. They are plotted as $R_{T/R_{273}}(=r_T^{-1})$ against the measured temperature in Fig. 2. It should be noted that below 4 K the pure crystal is not in the residual-resistance range. The insert ln Fig. 2 indicates a drop in R of approximately a factor of 1.9 between 4 and 1.4 K. In the case of the alloyed crystals, the small temperature dependence will prove to be of not much significance for the interpretation of the results.

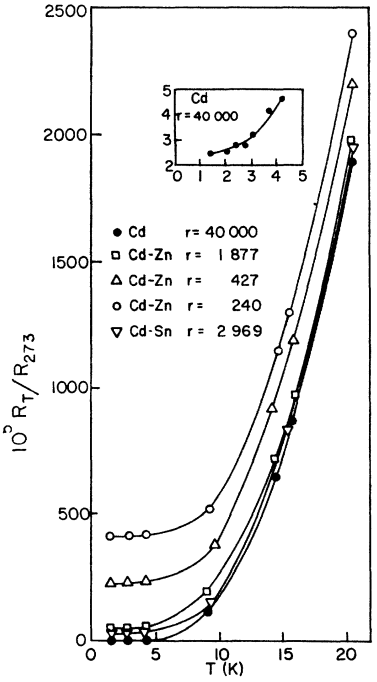

FIG. 2. Temperature dependence of R_T/R_{273}. Impurity concentrations are indicated by the residual-resistance ratio r.

A. Transverse Magnetoresistance

The experimental data on the transverse magnetoresistance are plotted in a reduced Kohler diagram in Fig. 3 which is similar to the one reported in the literature.[6] The solid lines in Fig. 3 represent the data for the pure cadmium crystal. The data points for Cd-Zn alloys are in general close to this line, but those for the Cd-Sn alloy taken below 4.2 K seem to deviate considerably. The Kohler plot in the range $r_TH=10^3$ kG to 10^4 kG exhibits a double curvature, with the inversion being around 3×10^3 kG. Above 10^4 kG the slope of the curve increases from 1.7 to 1.9. Taking the mean free path[10] of 1 mm in a sample with $r=30\,000$ and the Fermi velocity[4] equal to 1.63×10^8 cm sec^{-1}, $r_TH=10^4$ kG corresponds to $\omega\tau=3.6$.

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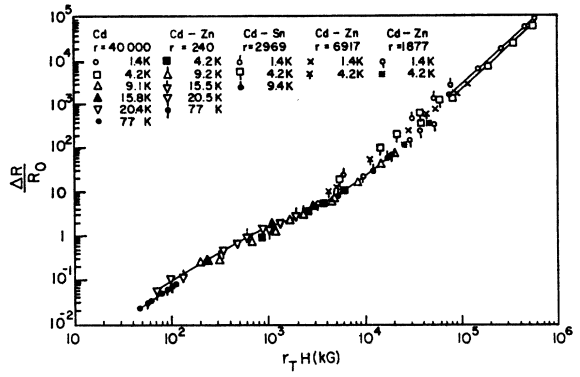

FIG. 3. $\Delta R/R_0$ $\{=[R(H,T)-R(H=0,T)]/R(H=0,T)\}$ against r_TH. The solid lines in the figure connect the data for the Cd sample.

B. Hall Resistivity

The Hall resistivity values ρ_{21} are shown in Fig. 4. In pure Cd, ρ_{21} changes sign from negative to positive at approximately 3.7 K. In Cd-Zn crystals there is a sign reversal in ρ_{21} at constant temperature for a certain field H_0 which is larger for higher Zn concentrations. At higher temperatures ρ_{21} remains positive. At 77 K ρ_{21} is approximately proportional to H and there is no practical difference between the Hall resistivities of the pure and the alloyed crystals. In Fig. 5, ρ_{21} taken from $\rho_{21}(H)$ curves is plotted for a field value of 20 kG against the temperature. The variation of H_0 for different impurity contents at 1.4 K is illustrated in Fig. 6.

For pure Cd, ρ_{21} changes from -700 to 200 (in units of 10^{-11} Ω m) from 1.4 to 5 K followed by a change of only a factor of 2 in magnitude for the same factorial increase of temperature from 5 to 20 K. Offhand the temperature for which ρ_{21} changes from negative to positive in a given field varies rather erratically with impurity content.

From Figs. 4–6 it can be deduced that there is no obvious relationship between ρ_{21} and r_TH (or $\omega\tau$). This is demonstrated more clearly when ρ_{21} is plotted against r_TH. Figures 7(a) and 7(b) depict $\rho_{21}>0$ for $0<r_TH<10^4$ kG and ρ_{21} for values of r_TH up to $\sim 4\times 10^5$ kG, respectively. From these figures it is indeed clear that a simple relation between ρ_{21} and r_TH (i.e., $\omega\tau$) does not exist at low temperatures in a manner similar to the Kohler relation for the magnetoresistance. In fact, for r_TH of the order of 10^5 kG (i.e., $\omega\tau\approx 36$) and $T=1.4$ K [Fig. 7(b)] the Hall resistivity is negative for both the pure sample and the alloys, but the magnitude for the alloys is larger by a factor of 20. Such a result might be considered conceivable if the Cd-Zn alloys were to have e/a larger than that for pure Cd, as is the case for the Cd-Sn alloy. For values $r_TH<3\times 10^3$ kG (i.e., $\omega\tau<1$), ρ_{21} is positive for the Cd-alloy crystals. The positive values for Cd were also observed at $T>3$ K, but below this temperature the small voltages at the low fields ($\sim$0.1 kG) were below the limits of the sensitivity of the measuring equipment.

At higher temperatures the effect of impurities is very small, as can be seen for the 20 K data in Fig. 7(a). The data for Cd-Sn are also fairly well described by the same curve at 20 K, albeit with consistently slightly lower positive values.

IV. CONCLUSIONS

From the summarized results as described, the following features present themselves:

(1) At temperatures of the order of 20 K and above $\rho_{21}(H)$ depends on temperature, but the effect of different Zn concentrations has disappeared. An increase in the e/a ratio, as seen for the Cd-Sn sample, reduces the positive values of ρ_{21} to a certain extent. Since at these temperatures the phonon scattering is expected to be larger than the impurity scattering, a relatively reduced effect of impurity concentration is plausible.

(2) Below 4 K there is a clear difference between the influence of impurity and temperature on the magnitude and the variation of ρ_{21}. (a) At a fixed temperature, such as 1.4 K, the sign of ρ_{21} changes at a field H_0 whose magnitude depends on the impurity concentration. It is interesting to note that for presumably very pure Cd a value $H_0<2$kG has been observed.[5,11] The product rH_0 varies from the order of 13 000 kG (for $r=6917$) to 5100 kG (for $r=427$) which corresponds to $4.7\geq\omega\tau\geq 1.8$. This crossover field and the $\rho_{21}(H)$ curves do not change in that temperature range in which the sample is in the residual-resistance range. (b) For a given field the sign reversal occurs for different concentrations at slightly different temperatures (4–6 K), but for the sample with the largest Zn concentration ($r=240$) no sign reversal occurs up to 25 kG. An increase in e/a moves this reversal to a much larger temperature.

(3) A representation of the results for ρ_{21} in terms of a single τ fails.

(4) On the other hand, the magnetoresistance $\Delta R/R_0$ can be represented by a Kohler diagram with a variation of n; $\Delta R/R_0\propto H^n$, with $n<1.9$ for $r_TH<10^4$ kG and $n\approx 1.9$ for above this value. It should be remarked that the deviation from the Kohler line for the pure Cd occurs for all samples below 4 K, where $\omega\tau>1$.

The results cannot all be simply explained from the published properties of the Fermi surface for Cd[12–20].

[11] A comparison is difficult since the authors (Ref. 5) do not indicate the purity of the Cd sample in terms of r. The assumption of higher purity is based on the magnitude of the reported oscillatory effects in ρ_{21}.

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[17] E. Alekseevskii and P. Gaĭdukov, Zh. Eksperm. i Teor. Fiz. **43**, 2094 (1962) [English transl.: Soviet Phys.—JETP **16**, 1481 (1963)].
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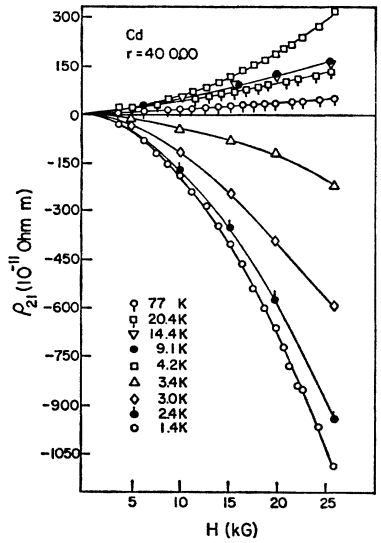
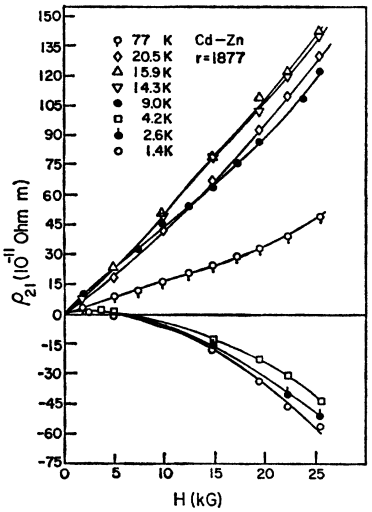


(a)



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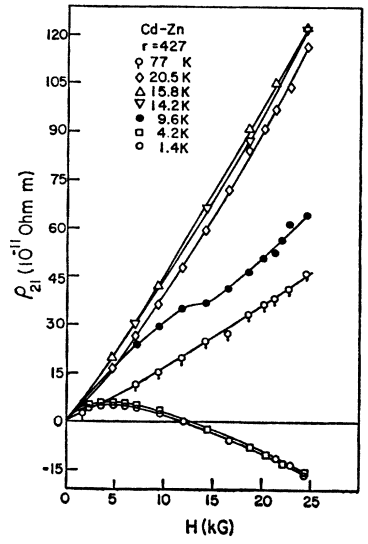

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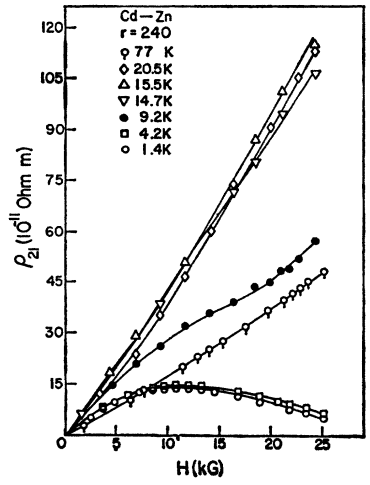

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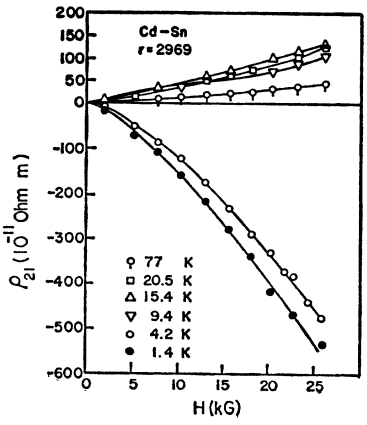


(e)

FIG. 4 (a)–(e). Temperature and magnetic field dependence of Hall resistivity ρ_{21}.

In any plane $\perp[0001]$, cadmium is considered to be a completely compensated metal. Its positive Hall resistivity can be considered to be a result of a balance between the electron and the hole contributions when the hole mass is the lowest.[21] Indeed, for Cd the mass of the electrons is larger than the masses of the holes.[18,22,23] Only closed orbits are possible in these planes. Such orbits lead to $\rho_{21} \propto H$ and $\Delta R/R_0 \propto H^2$ behavior. Magnetic breakdown effects can occur at the zone boundary and they have been observed[19] between the hole surfaces in the first and second zones above 30 kG. This breakdown will not cause any change in the character of the hole orbits and cannot account for the sign reversal in ρ_{21}.

It is possible to describe $\rho_{21}(H,T)$ curves with the two-band formalism,[24,25] using the ratios between the electron and hole concentrations or between their mobilities as adjustable parameters. As the expression for ρ_{21} contains terms of the difference between the products of concentration and mobility, the parameters can be adjusted to account for the sign reversal. Computer analysis of the data showed that these descriptive parameters were inconsistent and, therefore, could not indicate an acceptable physical interpretation. A more consistent result was obtained when besides an adjustable mobility ratio, a field-dependent scattering parameter [such as $\tau^{-1}=\tau_0^{-1}(1+aH)$] was introduced. The shape of the $\rho_{21}(H,T)$ curves could be represented reasonably well and the variation of the coefficient a indicated a more or less consistent temperature and impurity concentration dependence. The analysis, however, is not acceptable for several reasons. Not only is the concept of a field-dependent scattering time incompatible with its generally accepted definition, but

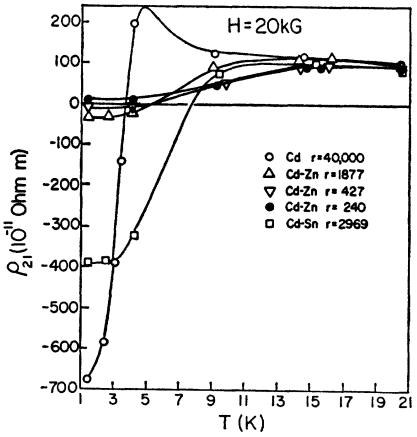


FIG. 5. ρ_{21} at 20 kG (taken from Fig. 4) against temperature.

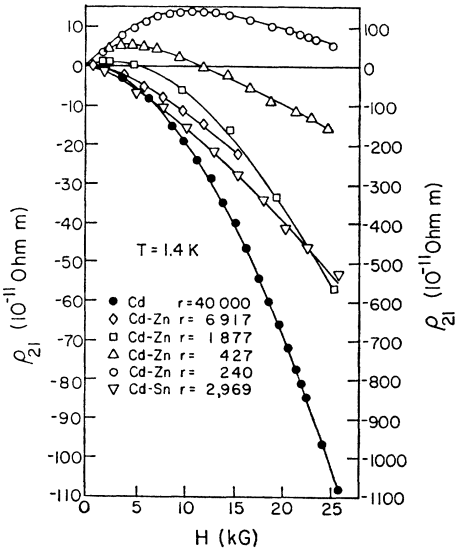
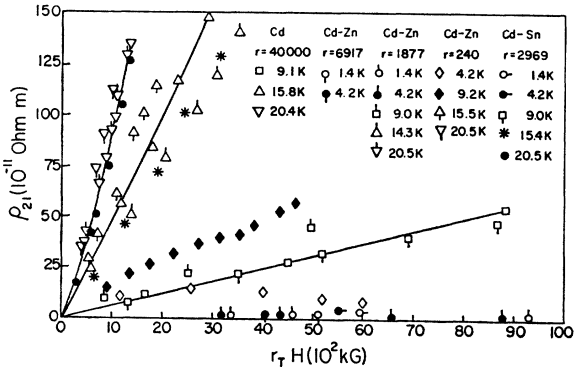


FIG. 6. ρ_{21} at 1.4 K against magnetic field. The right scale for ρ_{21} refers to Cd ($r=40\,000$), Cd-Zn ($r=6917$), and Cd-Sn ($r=2969$) while the left scale applies to Cd-Zn ($r=1877$), Cd-Zn ($r=427$), and Cd-Zn ($r=240$).



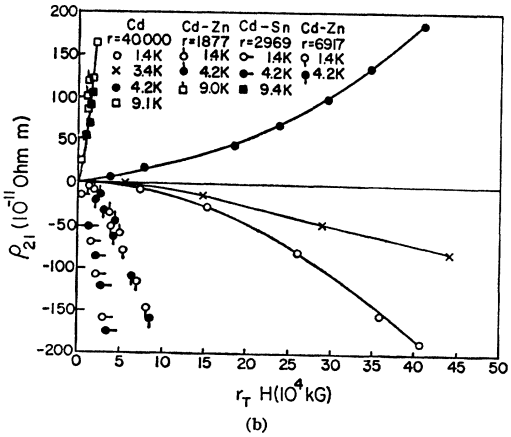


FIG. 7. (a) and (b) ρ_{21} versus $r_T H(\propto \omega\tau)$. The lines in the figures connect the results for the Cd sample.

the analysis leads to ρ_{21} remaining negative at 1.4 K for $H\rightarrow\infty$. There is experimental evidence[4] that Cd with approximately twice the present r value exhibits

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[22] O. P. Katyal, A. N. Gerritsen, J. Ruvalds, Richard A. Young, and L. M. Falicov, Phys. Rev. Letters 21, 694 (1968).
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a $\rho_{21}(H)$ curve which at low temperatures bends towards the $\rho_{21}=0$ line at about 13 kG. But if anything, the analysis indicated that an attempt to find an interpretation of the observed behavior as an effect in the relaxation time rather than as field- or temperature-dependent variations in the carrier concentrations or their mobilities might be more successful. In a preliminary publication,[22] the concept of scattering between adjacent sheets of the second-zone hole surface has been suggested as a possible explanation for the observed behavior of the Hall resistivity. In a following paper,[23] a discussion of this kind of scattering will demonstrate that the observed relations, as reported here and in the literature, between ρ_{21} and the parameters temperature, field, and impurity content (with no variation in e/a) can be derived in a formal manner. This approach requires the introduction of one adjustable parameter only, namely, the intersheet scattering time $\mathcal{T}$, the inverse of which is a measure of the probability for this scattering to occur. The sign reversal is a consequence of the intersheet scattering. Some discrepancies remain. Though the deviations from the Kohler relation $\Delta R/R_0=AH^n$ can be explained, the reason for the observed change in n that occurs between low and high $\omega\tau$ regions in particular remains unsolved. Further, the formalism is not very accessible to a quantitative test. The concept of intersheet scattering and the result of its formal discussion, however, suggest the variation of ρ_{21} with hydrostatic pressure.

It has been known[26,27] that under sufficient large hydrostatic pressure the Fermi surface of Cd is transformed into a surface similar to that of Zn by the disappearance of the gap between the adjacent sheets of the second-zone hole surface. Recent results [28] support this. Under pressure a continuous increase of the second-zone hole surface areas cut by the ΓKM plane is indicated. This increase in area would lead to a smaller gap distance between two adjacent sheets. Consequently, this would induce an enhanced intersheet scattering probability and a lower $\mathcal{T}$. The formal discussion[23] describes the net ρ_{21} value as the sum of two parts: (a) the holelike difference between the electron and hole contributions (compensated in number of carriers but having a hole character because of the much lower hole mass) and (b) the contribution of the intersheet scattering which has an electron character because the scattering results in the occurrence of electron orbits. In a magnetic field contribution (a) reaches a maximum for small $\omega\tau$ and approaches zero for large $\omega\tau$ values, and (b) increases continuously with $\omega\mathcal{T}$ for not too large values of ω. It is obvious that under equal circumstances a decrease in $\mathcal{T}$ will shift a $\rho_{21}(H)$ curve to higher fields. This is what was observed (Fig. 8) when a pure Cd sample was subjected to a hydrostatic pressure in an ice bomb. The behavior is similar to the effect of an increase in impurity content. Even though this result has been predicted more by deduction rather than by direct proof, it seems to be consistent within the line of thought. The similarity between the effects of pressure and impurities on the intersheet scattering is a point of interest and requires further investigation.

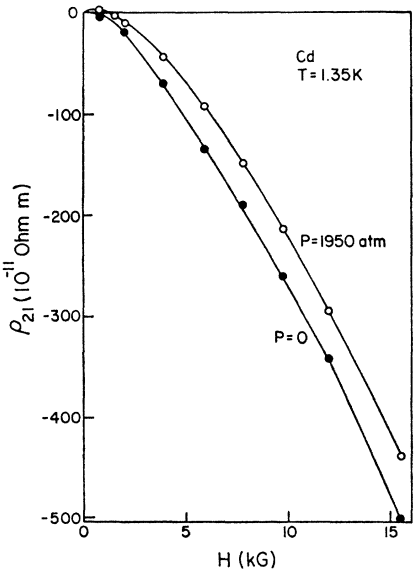

FIG. 8. Effect of hydrostatic pressure on ρ_{21} of a Cd sample at 1.35 K.

As a final conclusion, we are inclined to state that the present investigation has demonstrated a certain consistency in the behavior of ρ_{21} in relation to external parameters and that these relations indicate that the concept of a single static scattering time may have to be abandoned for certain special cases. Notwithstanding the summary character of the formal development of the concept of intersheet scattering, this concept could be used for a qualitative prediction of the dependence of ρ_{21} on an external parameter which was not considered in the construction of the formal description.

ACKNOWLEDGMENTS

We are indebted to Dr. R. W. Johnson of the James Franck Institute (University of Chicago) for the analysis of some of the samples and to Professor H. J. Yearian for his cooperation with the crystallographic checks and alignments by x-rays. We wish gratefully to acknowledge many helpful discussions with Professor L. M. Falicov, Dr. J. Ruvalds, and Dr. R. Young; we also wish to thank D. G. Seiler for the use of his ice-bomb apparatus for the hydrostatic-pressure measurements.

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[28] J. E. Schriber and W. J. O'Sullivan, in Proceedings of the Eleventh International Conference on Low-Temperature Physics, St. Andrews, Scotland, 1968, Abstract C4.6 (to be published).