

The integer p was then examined to separate even and odd y_p of (A-4) and of (A-5); y_0 and y_n were further separated from the even y_p . The y_p of (A-4) were accumulated to give:

$$\sum \text{even } y_p, \quad (\text{A-6})$$

$$\sum \text{odd } y_p, \quad (\text{A-7})$$

$$\sum (y_0 + y_n). \quad (\text{A-8})$$

A similar accumulation was done for the y_p of (A-5). When a test of p indicated that all y_p of (A-1) had

been calculated, the accumulation (A-6) was multiplied by the factor $2h/3$. The accumulation (A-7) was multiplied by $4h/3$. These products were then added to the sum of $y_0 + y_n$ to give K . Similar steps produced $2\pi^{-\frac{1}{2}}L$.

The integrals for the thermoelectric function, $K^{(2)}(\beta, \gamma)$, were calculated in the same manner as the conductivity integrals, using 400 intervals over the range 0-25. Results agreed to five significant places with a recalculation using 400 intervals over the range 0-50.

Hall Effect in Titanium, Vanadium, Chromium, and Manganese*

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(Received June 14, 1957)

The Hall effect in Ti, V, Cr, and Mn has been measured at room temperature with fields up to 30 kilosterds. The Hall constant was positive for all of these elements. The effect is extremely small in Ti and apparently sensitive to small amounts of impurities. The results for these transition elements indicate that electrical conduction is predominantly due to hole conduction.

I. INTRODUCTION

THE complex nature of the transition elements has generally limited calculation of their band structure although some detailed calculations for copper,¹ nickel,² and iron³ have been made. Because of the approximations introduced, only qualitative comparisons with experiments can be made. Usually these calculations are extrapolated to the nonferromagnetic transition elements for purposes of discussion. The general feature is a complex $3d$ band structure with a high density of states and thus a low mobility. This result agrees with both the magnetic properties and the electronic specific heat. Electrical conduction is generally considered to arise from the $4s$ electrons because of the low mobility of the $3d$ electrons. Since the Hall effect allows estimates to be made of the number of conducting particles per unit volume and their sign, this unique measurement is useful for examining some details of the band structure.

Recent measurements in the Cu-Ni⁴ alloys and the

Co-Ni⁵ alloys have demonstrated that electrical conduction is predominantly due to the $4s$ electrons; however, the results of Armco iron⁶ indicated predominant hole conduction. The increased interest in the transition elements and the availability of pure materials led to the Hall measurements described in this paper.

A brief summary of the results for Ti, V, Cr, and Mn has been given earlier.⁶ The method of measurement is that described previously.⁵ Unless specified, the sample dimensions were 6.0 cm × 1.00 cm × 0.100 cm and carried a current from 10 to 20 amperes. Whenever possible, chemical analyses of the samples are given since some of the results may be sensitive to small impurities.

II. EXPERIMENTAL RESULTS

1. Titanium

Three titanium samples were investigated, designated below as I, II, and III. Samples I and II were obtained from a commercial bar of material. Sample I was measured after machining whereas sample II was vacuum-annealed at 600°C for two hours and slowly cooled to room temperature before measurements were made. Sample III⁷ was vacuum-annealed at 800°C for 6 hours and slowly cooled to room temperature. Considerable care was exercised to avoid contamination

* This work was supported in part by the U. S. Atomic Energy Commission and the Office of Naval Research.

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¹ H. M. Krutter, *Phys. Rev.* **48**, 664 (1935); J. C. Slater, *Phys. Rev.* **49**, 537, 931 (1936).

² G. C. Fletcher and E. P. Wohlfarth, *Phil. Mag.* **42**, 106 (1951); G. C. Fletcher, *Proc. Roy. Soc. (London)* **65**, 192 (1952); G. F. Koster, *Phys. Rev.* **98**, 901 (1955).

³ M. F. Manning, *Phys. Rev.* **63**, 190 (1943); J. B. Greene and M. F. Manning, *Phys. Rev.* **63**, 203 (1943).

⁴ A. I. Schindler and Emerson M. Pugh, *Phys. Rev.* **89**, 295 (1953).

⁵ S. Foner and Emerson M. Pugh, *Phys. Rev.* **91**, 20 (1953).

⁶ S. Foner, *Phys. Rev.* **91**, 447(A) (1953).

⁷ D. S. Billington of the Oak Ridge National Laboratory provided this sample and obtained the chemical analysis of the three samples investigated.

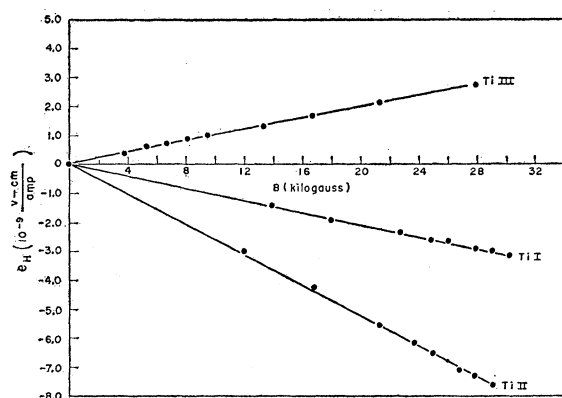


FIG. 1. Hall effect of three titanium samples at room temperature.

during the preparation of this sample. The chemical analyses for these samples are given in Table I.⁷ The potential difference per unit current, per unit thickness, e_H , versus magnetic induction, B , is shown in Fig. 1 for these samples. The magnitude and sign of the effect depend on the particular sample investigated. A small Hall effect for Ti has also recently been observed by Juretschke.⁸ The positive and somewhat higher Hall constant obtained by Scovil⁹ may be due to differences in the impurities.

2. Vanadium

The results for vanadium¹⁰ are shown in Fig. 2. The Hall effect is positive and considerably larger than in Ti.

3. Chromium

The chromium sample was cut from the ingot used by Friedberg *et al.*¹¹ for electronic specific-heat measurements. The current leads were soldered to a thin nickel

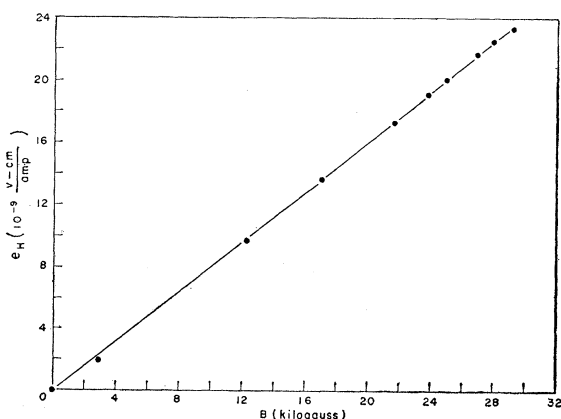


FIG. 2. Hall effect of vanadium at room temperature.

⁸ H. J. Juretschke (private communication), Polytechnic Institute of Brooklyn, New York.

⁹ G. W. Scovil, *J. Appl. Phys.* **24**, 266 (1953).

¹⁰ Furnished by the Vanadium Corporation of America.

¹¹ Friedberg, Estermann, and Goldman, *Phys. Rev.* **85**, 375 (1952) and **87**, 582 (1952).

film plated on the ends of the sample which was 2 cm × 1 cm × 0.110 cm. Chemical analysis of this sample showed it to be 99.9% pure Cr. An x-ray analysis¹² of this sample showed that the Cr sample was body-centered cubic. The results for this Cr sample are shown in Fig. 3.

During the measurements on this sample it was found that the Hall effect seemed to vary strongly with temperature. This effect was examined over a limited range of temperature by varying the magnet cooling and sample current. The results, shown in Fig. 4, show a decrease in Hall constant with increasing temperature. Over this limited range of temperatures the effect is linear and about 1% per degree centigrade. Because of the limited range of temperatures investigated, these results should be considered as only qualitative data. Examination of the Hall effect over a much wider temperature range would be desirable.

4. α -Manganese

A sample of α -manganese^{12,13} was used for the Hall measurements. The sample, of electrolytic flake origin,

TABLE I. Chemical analysis of titanium samples.^a

A. Vacuum fusion gas analysis ^b						
Sample	O ₂	N ₂	H ₂			
I	0.042	...	0.0015			
II	0.017			
III	0.010			
B. Spectroscopic analysis of metallic impurities ^c						
Sample	Fe	Ni	C	Mn	Mg	Cr
I	0.06	<0.01	0.025
II	0.047	<0.01	0.024
III	0.092	<0.01	0.01	<0.001	<0.001	0.015

^a Units: impurities in percent by weight.

^b Gases not detected are indicated by a dash.

^c Elements not analyzed are denoted by

was deoxidized in dilute HCl, annealed at about 400°C for H₂ degassing, and stored in an atmosphere of He until used. Spectroscopic analysis showed a trace of Ca and Cu (less than 0.01%) and faint traces of Fe, Mg, and V. No oxide lines were visible in the neutron-diffraction pattern unless surface oxidation was present in a finely divided form.¹³ The same material was used by Guthrie *et al.*¹⁴ for electronic specific-heat measurements. The electrolytic flake was quite small, 1.54 cm × 0.61 cm × 0.065 cm. To avoid contamination, pressure contacts for the primary current were used. Contact problems were minimized by using point contacts for these leads and currents below 4 amperes. The results of measurements on this sample are shown in Fig. 5. The sign of the Hall effect disagrees with that obtained

¹² Mrs. Sylvia Couling, formerly of the Carnegie Institute of Technology, Department of Metallurgy, provided the x-ray analysis of both the Cr and Mn samples.

¹³ C. G. Shull of the Oak Ridge National Laboratory provided the α -manganese sample and the spectroscopic analysis.

¹⁴ Guthrie, Friedberg, and Goldman, *Phys. Rev.* **98**, 1181(A) (1955).

by Zahn and Schmidt¹⁵ for Mn; however, Frank¹⁶ has suggested that a positive value is expected from the work of Justi and Kohler¹⁷ on Re.

III. DISCUSSION OF RESULTS

A tabulation of the room-temperature Hall constants is given in Table II, where R_0 is the ordinary Hall constant, n^* the effective number of electrons per atom, and γ the electronic specific heat. Room-temperature Hall constants are plotted in Fig. 6. The detailed structure of this curve between Cu and Ni and between Ni and Co has been obtained from measurements at room temperature on a series of Cu-Ni alloys⁴ and on a series of Ni-Co alloys.⁵ Measurements on two Fe-Ni alloys¹⁸ are not shown but they fit reasonably well on this curve of R_0 versus electrons per atom. Since measurements have not yet been completed on any of the other alloy systems, straight lines have been drawn between the points representing the Hall constants for the elements.

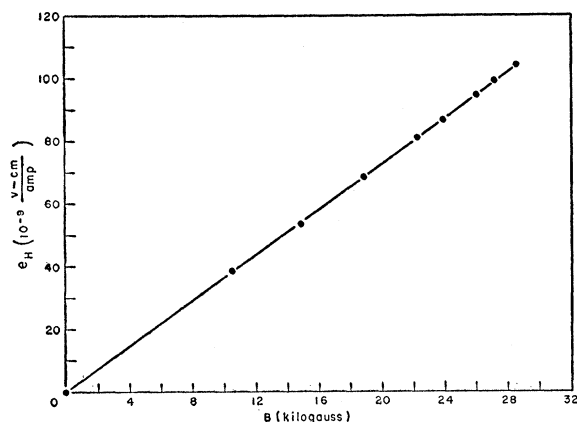


FIG. 3. Hall effect of chromium at room temperature.

More recently the Cu-Ni alloys have been studied over a wide range of temperatures.^{19,20} For these alloys it has been shown²⁰ that the detailed temperature dependence can be explained on the basis of a relatively simple band²¹ model. An analysis of present data along these lines is unfortunately not possible, if only for the reason that Ti, V, Cr, and Mn are not ferromagnetic.

If we assume as in the ferromagnetic metals, non-interacting, conducting 4s and 3d bands which have relaxation times similar to those expected in ferro-

¹⁵ H. Zahn and H. Schmidt, Deut. Phys. Gesell. Verh. 9, 98 (1907).

¹⁶ Professor V. Frank (private communication), Technical University of Denmark, Copenhagen.

¹⁷ E. Justi and M. Kohler, Braunsch. Wiss. Gesell. Abh. 3, 44 (1951).

¹⁸ S. Foner, Phys. Rev. 99, 1079 (1955).

¹⁹ Philip Cohen, doctoral dissertation, May, 1955, Carnegie Institute of Technology, Pittsburgh, Pennsylvania (unpublished).

²⁰ F. E. Allison and Emerson M. Pugh, Phys. Rev. 102, 1281 (1956).

²¹ Emerson M. Pugh, Phys. Rev. 97, 647 (1955).

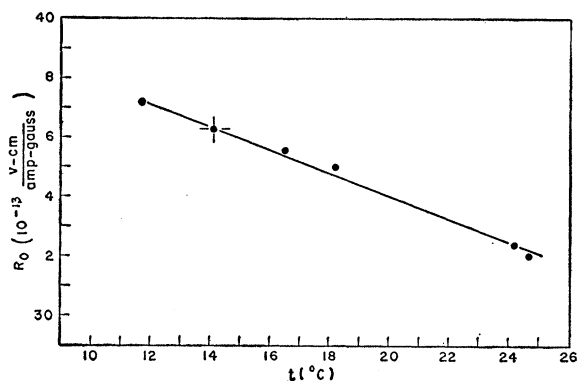


FIG. 4. Temperature dependence of R_0 for chromium over a limited range of temperature.

magnetic metals, we can make general statements concerning the predominant conduction based on the electronic specific-heat data shown in Table II. A large γ indicates a high density of states in the 3d band, and thus a low mobility of these carriers. The positive Hall constant then requires that: (1) either the hole conduction is due to the 3d band, in which case there must be no 4s electrons present because if any high-mobility 4s electrons were available the low-mobility 3d holes would not be observable; or (2) high-mobility 4s-band holes are present, in which case the 3d hole contribution again would be negligible. Because these two possibilities are speculative, only the second is discussed here.

Conduction due to 4s-band holes requires that the Fermi level be near the top of the 4s band. This is not unreasonable since one expects the 3d band to become wider [$N(\epsilon)$ to decrease] as one goes from Ni toward Ti. A discussion of this effect and the modifications of earlier work to include the body-centered cubic structures is given by Slater in a recent report.²² He points

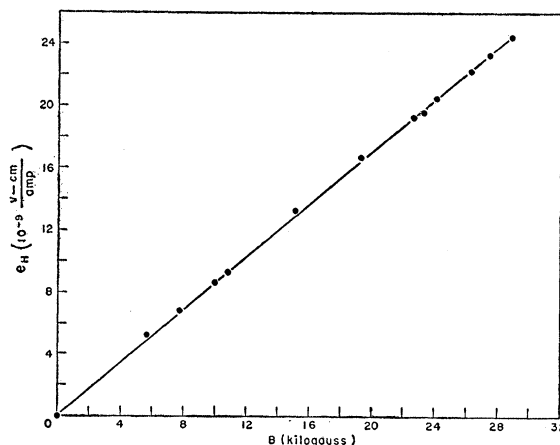


FIG. 5. Hall effect of manganese at room temperature.

²² J. C. Slater, Massachusetts Institute of Technology, Solid State and Molecular Theory Group Technical Report 6, April 15, 1954 (unpublished).

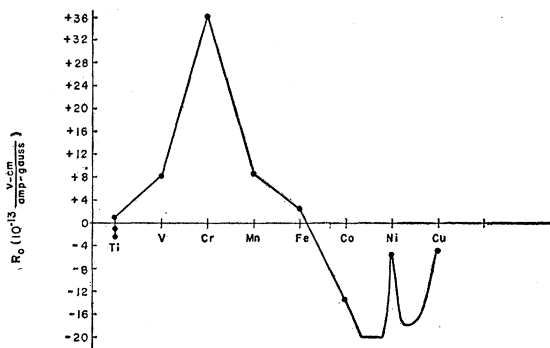


Fig. 6. Hall constants of various $3d$ transition elements at room temperature. See text for discussion of shape of curve.

out that the dip in the density of states curves near Cr is a consequence of the calculations for the body-centered structures. Even though the $3d$ band becomes wider, the specific-heat measurements (see Table II) indicate that the densities of states for the elements are quite large (except for Cr), thus the $4s$ carriers, if present, should be predominant in the Hall effect. The recent indications of s -electron concentrations (and possible p contributions at high concentrations) exceeding 1.0 for Fe as suggested by Stoner and recently confirmed by Coles,²³ and perhaps increasing as the atomic number decreases, indicate that the positive values of R_0 for Fe, Mn, Cr, and V are reasonable if d -band conduction were negligible.²⁴

The positive and negative R_0 's for the different Ti samples are difficult to explain. Although the magnitudes as shown in Fig. 1 are small, they are certainly outside the experimental errors. The results seem to de-

²³ E. C. Stoner, Proceedings of the Grenoble Conference (unpublished); B. R. Coles (private communication).

²⁴ Note added in proof.—The possibility of $3d$ band conduction is not completely eliminated. Recent x-ray scattering experiments by R. J. Weiss and J. deMarco (International Conference on Current Problems in Crystal Physics held at M.I.T., Cambridge, July 1–5, 1957) indicate only $0.2 \pm 0.4d$ electrons are localized on the Cr metal atoms and only $2.3 \pm 0.3d$ electrons are localized on the Fe metal atoms. If this is true, one might expect the remaining d electrons to contribute to electrical conduction. No detailed interpretation can be given at this early date. It is interesting to note, however, that R_0 is positive for Fe and Cr but negative for Cu, Ni, and Co where the x-ray results are as expected.

TABLE II. Tabulation of Hall effect in $3d$ transition elements.

Element		$(10^{13} \times R_0 \text{ v-cm/amp-gauss})$	n^*	t ($^{\circ}\text{C}$)	$10^4 \times \gamma$ (cal/deg ² /mole)
Ti	I	-1.06	10.4	...	8.3 ^a
	II	-2.59	4.3	18	
	III	+1.02	-10.8	21	
V		+8.20	-1.09	28	9.3 ^b
Cr		+36.3	-0.23	14	3.74 ^a
Mn		+8.44	-0.91	24	42 ^c
Fe		+2.45	-3.02	13	12
Co		-13.3	0.53	14	12
Ni		-5.6	1.2	9	17

^a See reference 11.

^b Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).

^c See reference 15.

pend on the purity but also may depend on the methods used in the preparation of the particular sample measured. The chemical analyses, shown in Table I, do not correlate directly with the sign of the effect. The small R_0 may be due to the balancing effect of both holes and electrons in the overlapping $4s$, $4p$, and $3d$ bands.

IV. SUMMARY

The Hall effect in Ti, V, Cr, and Mn has been measured at room temperature. The effect is linear with magnetic field and positive in these transition metals. The results can be qualitatively interpreted using simple band models; however, some ambiguity results because a measure of the $3d$ -band holes is not available. This ambiguity is not present in the ferromagnetic transition elements because measurements of the saturation moment give this information. The positive effect in Ti is quite small and may be reversed by small impurities.

ACKNOWLEDGMENTS

The author is indebted to Professor Emerson M. Pugh, Professor J. E. Goldman, Dr. N. Rostoker, and Dr. Bryan R. Coles for many valuable discussions, to Mrs. A. Watson for her generous assistance with the computations, to the various laboratories for supplying the samples, and to the U. S. Atomic Energy Commission and the Office of Naval Research for support of this investigation.