

## Measurements of the Hall Effect and Resistivity in Pyrrhotite\*

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Hall-effect and resistivity experiments were carried out on natural crystals of pyrrhotite, in the temperature range from 77 to 450°K. Because of the magnetic anisotropy, samples were cut and measured in three different orientations of the hexagonal crystals. For samples cut with their long axis perpendicular to the  $c$  axis and with the magnetic field applied parallel to the  $c$  axis (paramagnetic case), the sign of the Hall coefficient changes from  $n$  to  $p$  type with increasing temperature. The reversal takes place at 165°K. The Hall coefficient in the exhaustion range has a value  $\sim 10^{-2}$  cm<sup>3</sup>/C which corresponds to  $10^{20}$  cm<sup>-3</sup> carrier concentration. For samples with both their long axis and the magnetic field perpendicular to the  $c$  axis (ferromagnetic case), no reversal of the Hall coefficient was observed and the material was  $p$  type for all temperatures. The curve of the Hall resistivity  $\rho_H$  versus the magnetic induction, for constant temperature, exhibits the typical form for ferromagnetic materials.

### INTRODUCTION

#### Structure of the Material

THE composition of pyrrhotite is described by the formula  $\text{Fe}_7\text{S}_8$ , which implies the existence of excess sulphur atoms beyond the stoichiometric composition  $\text{FeS}$ . Because of the magnetic anisotropy of the material, the interest of Weiss<sup>1</sup> and many others<sup>2,3</sup> was attracted to it. Measurements have been carried out on the magnetic properties (magnetic susceptibility for various sulphur contents, temperatures, and crystallographic directions). The measurements were done partly on natural crystals and partly on synthetic (polycrystalline) ones.

Pyrrhotite forms hexagonal crystals having the  $\text{NiAs}$  structure. The structure perpendicular to the  $c$  axis is considered to consist of parallel planes, occupied alternately by sulphur and iron atoms. Not all iron planes are equivalent because (a) some iron sites are empty, as follows from comparison of the measured and computed densities, and (b) both ferrous  $\text{Fe}^{2+}$  and ferric  $\text{Fe}^{3+}$  ions are present. In the stoichiometric composition only ferrous ions are present, but beyond this, as a deficiency of iron atoms occurs progressively, ferrous ions turn to ferric ions, so that the excess sulphur atoms are doubly ionized. Based on the measured saturation magnetization, we assume unequal distribution of the ferric ions on the successive lattice planes. Because of this difference in distribution, we have two sublattices within the cation lattice, made up of the odd- and even-numbered iron planes, respectively. Further, x-ray investigation proves the existence of a superlattice which is made up of nine iron planes with the associated sulphur planes and has a period  $4c$ . According to the accepted structure of pyrrhotite, as inferred from the value of saturation magnetization, the empty sites are located in that particular sublattice in which the ferric

ions are also located. The superstructure disappears for composition near the stoichiometric one.

#### Magnetic Properties

Along the direction parallel to the  $c$  axis, the crystal is paramagnetic, while perpendicular to the  $c$  axis and within the so-called "magnetic plane," the crystal is ferromagnetic. In the magnetic plane the ease of magnetic saturation varies with the direction. The saturation magnetization is very small, of the order of 80 emu, which corresponds to a magnetic moment per iron atom of the order of  $\frac{1}{4}\mu_B$ . The smallness of this value implies that the material is ferrimagnetic.

According to Néel<sup>2</sup> the interaction between neighbor iron ions causes the parallel orientation of the magnetic moments within the same plane, but antiparallel orientation between successive planes. This effect combined with the differentiation of the two sublattices produces the ferrimagnetic nature of pyrrhotite. As the composition approaches the stoichiometric one ( $\text{FeS}$ ), the superstructure disappears, the two sublattices become equivalent and the material is, antiferromagnetic.

A recent measurement<sup>4</sup> of the gyromagnetic ratio gives a value in agreement with the one for ferromagnetic materials which corrects the old erroneous value<sup>5</sup>  $g=0.63$ . X-ray reflection measurements<sup>6</sup> also showed a regular magnetic behavior of pyrrhotite.

### MEASUREMENTS AND RESULTS

#### Samples and Experimental Apparatus

As far as the author is aware, there are no measurements of the electric properties of pyrrhotite. So we undertook the task of measuring the Hall effect and the resistivity in natural crystals. First we tested the samples at our disposal to see if they were single crystals

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<sup>1</sup> P. Weiss, *J. Phys.* **4**, 469, 829 (1905).

<sup>2</sup> L. Néel, *Rev. Mod. Phys.* **25**, 58 (1953).

<sup>3</sup> K. Yosida, *Progr. Theoret. Phys. (Kyoto)* **6**, 356 (1951).

<sup>4</sup> G. G. Scott and André J. P. Meyer, *Phys. Rev.* **123**, 1269 (1961).

<sup>5</sup> F. Coetierier, *Helv. Phys. Acta* **8**, 522 (1935).

<sup>6</sup> K. Alexopoulos and A. Theodossiou, *Proc. Phys. Soc. (London)* **B66**, 753 (1953).

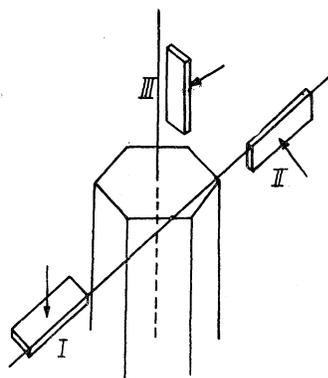


FIG. 1. Sample orientation for the three measured cases. The arrows show the direction of the magnetic field.

by taking Laue photographs. Then from Debye-Scherrer diagrams, and following the graphic method of Hull-Davey,<sup>7</sup> the lattice dimensions were determined. The values found are as follows:  $a = 3.43 \text{ \AA}$  and  $c = 5.74 \text{ \AA}$ . From the known change of the lattice dimensions against the sulphur content of the iron sulphides,<sup>8</sup> the composition of the samples was determined.

The present work consists of measurements both in the paramagnetic and ferromagnetic direction. Samples were cut so that the magnetic field could be applied parallel to the  $c$  axis (paramagnetic case, I), or perpendicular to it (ferromagnetic case, II and III). In case II, the sample current flows perpendicular to the  $c$  axis, while in case III it is parallel to it. Figure 1 shows the three different orientations of the samples.

In all cases the Hall effect and resistivity were measured in the temperature range from 77 to 450°K. From a large number of samples, only those were chosen for the measurements which showed sufficient homogeneity, as this could be tested from the voltage distribution along the sample. On the average only one of every five pieces was found convenient for the measurements.

Figure 2 gives the details of the crystal holder. Pressure probes were used for supplying the main current through the sample. In this way the construction permits the thermal expansion of the sample while assuring good contacts everywhere. The mechanical tension exercised parallel to the axis of the sample, because of the mounting, is of the order of  $10 \text{ Kgf/cm}^2$ . The springs of the two pistons and the four probe wires were of phosphor bronze. Tinned

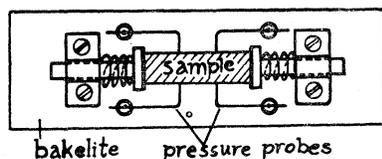


FIG. 2. Sample holder. The sample current is supplied by two piston electrodes, which insure good contact by the force of springs. Average sample dimensions:  $12 \times 4 \times 1 \text{ mm}^3$ .

<sup>7</sup> A. W. Hull and W. P. Davey, *Phys. Rev.* **17**, 549 (1921).

<sup>8</sup> H. Haraldsen, *Z. Anorg. Allgem. Chem.* **246**, 169 (1941).

copper plates were soldered at the ends of the two pistons, and these plates were found to insure good contact between crystal and current electrodes.

The cryostat is made of two chambers which can be evacuated separately and also filled with helium exchange gas. A heating coil surrounds the holder for the adjustment of the temperature, which is measured by a copper-constantan thermocouple.

Preliminary measurements with a polycrystalline sample indicated that the Hall voltage was very weak, of the order of a few microvolts. To improve the measurements, the sample current, supplied by batteries, was increased to  $\frac{1}{4}$  A. Higher current caused instability of the electric circuits. Under the working conditions, the magnet had a maximum field of 7000 Oe. The pole distance was about 50 mm and the pole diameter 10 cm, large enough in comparison with the length of the crystal to obtain a homogeneous field. All the voltages were measured by a K-3 (Leads-Northrup Co.) poten-

TABLE I. Hall-effect measurements of a paramagnetic sample.  $U$  is the voltage between Hall-effect probes in millivolts, and  $I$  is the sample current.

	$H$	Liquid-nitrogen temperature		
		$I$	$U$ (mV)	
A	+	+	-0.0908	$I = 246.5 \text{ mA}$ $H = 6850 \text{ Oe}$
B	-	+	-0.0809	
C	-	-	+0.1522	
D	+	-	+0.1627	
			$U_H = -5.1 \mu V$	
	$H$	Room temperature		
		$I$	$U$ (mV)	
A	+	+	-0.1700	$I = 250 \text{ mA}$ $H = 6850 \text{ Oe}$
B	-	+	-0.1717	
C	-	-	+0.1717	
D	+	-	+0.1697	
			$U_H = +0.9 \mu V$	

tiometer and galvanometer. The system had a sensitivity of the order  $0.5 \mu V/\text{mm}$ . In the measurements of the ferromagnetic sample, the galvanometer deviations were in the range 0-5 mm, and in the case of the paramagnetic sample, 0-15 mm. The error was of the order of  $\frac{1}{3}$  mm, which gives quite a large relative error. It was therefore necessary to repeat each set of measurements from each probe pair and to take the average value of the voltages.

### Measurements of the Paramagnetic Sample

We began with measurements of a sample of the paramagnetic case. The exact crystallographic orientation of the long axis of the sample was not known; however, it lies within the magnetic plane. In this case the electric field is perpendicular to the  $c$  axis, while the magnetic field is parallel to it. For the Hall measurements we followed the usual procedure, reversing the magnetic field and the sample current. For the resis-

tivity measurements the voltages were measured for both directions of the sample current, the value of which was found by measuring the voltage drop across a standard resistance. As an example of the measurements, we give a set of values on both sides of the sign reversal temperature in Table I. By combining the four voltages in the usual way, we eliminate several spurious voltages, such as the Ohmic drop, which is due to the misaligning of the probes on an equipotential surface. There still remains the Ettingshausen voltage, which reverses sign when the Hall voltage does so. As will be explained later, the voltage due to the Ettingshausen effect is considered to be negligible.

Figure 3 gives the Hall-effect coefficient against the reciprocal temperature. A second sample, cut from a different block, gave similar results. Reversal of sign of the Hall coefficient occurs at a temperature of about 165°K. At lower temperatures the sample is an *n*-type semiconductor, and after the reversal it becomes *p* type.

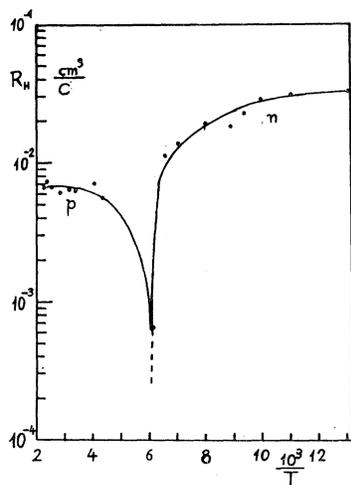


FIG. 3. Hall coefficient of a sample of case I. Magnetic field of 6850 Oe.

The sign of the Hall coefficient was determined from the known direction of the sample current, the magnetic field and polarity of the Hall voltage, and also by comparison with the sign of germanium samples with known impurities.

#### Measurements of the Ferromagnetic Samples

The procedure for Hall-effect measurements in ferromagnetic samples is quite different from and more complicated than in nonferromagnetic samples. But in a preliminary measurement we followed the same procedure as in the paramagnetic case and measured the Hall voltage versus temperature. For the calculation of the (single) Hall coefficient, the field  $\sim 7000$  G outside the sample was used. The sample was found to be *p* type throughout the temperature range. The ordinary procedure for ferromagnetic materials consists in measuring the Hall voltage against the applied magnetic field for a constant temperature. Each isotherm is

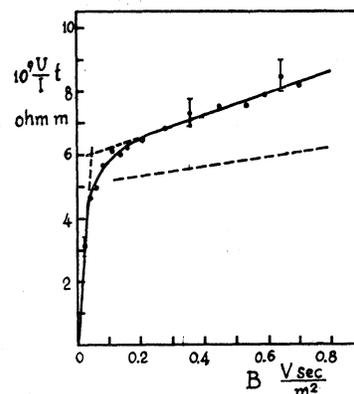


FIG. 4. Isotherm for 197°K. The broken line in the high-field range is corrected and gives the ordinary coefficient  $R_0$ . The vertical lines show the magnitude of error.

plotted as  $(U_H/I)t$  against  $B$ , where  $B$  is the magnetic induction inside the sample,  $I$  the sample current, and  $t$  the thickness of the sample. A difficulty arises here in calculating  $B$ , which necessitates knowledge of the demagnetizing factor  $N$ . The magnetic induction is given by the formula

$$B = \mu_0 H_e + J(1 - N).$$

If we accept  $N = 1$ , which is an approximation for the case of a thin disk perpendicular to the magnetic field, then we obtain  $B = \mu_0 H_e$ , where  $H_e$  is the undisturbed field, i.e., the field before inserting the sample, and  $\mu_0$  is the permeability of the vacuum. Here we neglect the fact that the magnetic field inside the sample is not homogeneous, because the demagnetizing field is smaller near the edge than in the center of the sample.<sup>9</sup>

As constant-temperature baths we used liquid  $N_2$ ,  $O_2$ ,  $CO_2$ , Freon 13, and ice; we also used the room temperature, and obtained several elevated temperatures by using the heater: 61, 116, and 151°C.

All the isotherms follow about the same trend. Typical is the curve of the room temperature isotherm as shown in Fig. 4. Each curve consists of two straight parts, the slopes of which determine the two Hall coefficients  $R_0$  and  $R_1$  (ordinary and extraordinary, respectively). Each point of Fig. 4 comes from the average of 12, and in some cases of 18, measurements. The basic formula describing the Hall effect in ferromagnetic materials, as given by Jan,<sup>10</sup> is

$$\rho_H = R_0 \mu_0 H + R_1 J,$$

where  $\rho_H$  is the Hall resistivity  $(U_H/I)t$ ,  $H$  the field inside the sample, and  $J$  the magnetization of the material. By substituting  $\mu_0 H = B - J$ , where  $B$  is the magnetic induction inside the sample, we obtain

$$\rho_H = R_0 B + R_s J, \quad (1)$$

where  $R_s = R_1 - R_0$ . The experimentally determined

<sup>9</sup> E. Tatsumoto and T. Okamoto, J. Phys. Soc. Japan 14, 975 (1959).

<sup>10</sup> J.-P. Jan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

TABLE II. Hall resistivity  $\rho_H$  (ohm m) ( $\times 10^9$ ) versus magnetic induction  $B$  and temperature  $T$ .

$BVs/m^2$	$T^\circ K$						
	197	245	277	297	335	389	423
0.020	3.07	3.13	2.92	3.43	2.74	3.14	1.27
0.040	4.65	4.63	3.82	4.10	4.25	3.70	2.26
0.060	4.95	4.93	4.97	5.06	4.64	4.10	2.79
0.086	5.61	5.95	5.55	6.00	4.94	4.85	3.13
0.106	6.18	5.88	5.85	6.47	5.29	5.43	3.54
0.134	5.98	6.90	5.61	5.43	5.43	5.46	3.34
0.152	6.18	7.37	6.62	7.03	6.01	5.18	4.07
0.203	6.44	7.45	7.38	7.41	5.53	5.86	3.85
0.273	6.81	8.02	8.18	7.63	6.18	6.56	4.42
0.350	7.29	8.59	8.05	8.08	6.16	6.71	3.97
0.443	7.50	8.33	8.42	8.11	6.77	6.38	4.65
0.533	7.53	9.40	9.26	7.98	7.41	6.95	4.82
0.587	7.84	8.24	8.78	8.70	6.72	6.94	5.00
0.638	8.42	9.23	9.22	8.52	6.87	7.06	4.87
0.695	8.13	9.57	8.98	9.40	6.99	7.91	5.21

curve ( $\rho_H \rightarrow B$ ) $_{T=\text{const}}$  consists of two linear sections, the intersection of which determines the value of the field where magnetic saturation begins. The determination of the two coefficients  $R_0$ ,  $R_1$  is obtained from the slopes of the two linear sections. By differentiating formula (1)

$$d\rho_H/dB = R_0 + R_s dJ/dB,$$

we find  $R_0$ , since  $dJ/dB=0$  beyond the magnetic saturation. To determine  $R_1$  two methods are used. The first method (a) requires only the upper section (high-field range) of the curve, which is extrapolated towards the vertical axis. Substituting  $B=0$  in formula (1),  $R_s$  can be determined, provided that the saturation magnetization of the material is known at the particular temperature of the measurements. As the magnetization curve of our particular samples is unknown, the determination of  $R_1$  was done by the second method (b), which consists in the calculation of the slope of the initial straight part. Well below saturation,  $\mu_0 H$  can be considered negligible, and then, according to the formula  $\mu_0 H = B - J$ ,  $B$  is practically equal to  $J$ . Now formula (1) reduces to  $\rho_H = R_1 B$ . Therefore  $R_1$  can be found from the slope of the initial straight part.

All the experimental data ( $\rho_H \rightarrow B$ ) for the ferromagnetic case, for seven different temperatures, are listed in Table II. The data for the  $O_2$  isotherm are not included because of the different field values used in this case. The largest available magnetic field was of the magnitude of 7000 Oe and the measurements were limited within this range. In one case measurements were extended up to 8500 Oe. Figure 5 gives the two coefficients  $R_0$  and  $R_1$  versus the reciprocal of the temperature.

### Resistivity Measurements

The order of magnitude of the resistivity is about the same for all the measured cases. It was found that samples from various parts of our block follow two

distinct trends versus temperature, irrespective of the crystallographic orientation. These trends are shown in Fig. 6 for samples of case I. In both of them no influence of the sign reversal can be seen. Similar curves occurred in case II, where three different samples were measured. In all cases the resistivity curve is smooth throughout the temperature range.

An attempt was made to measure the magneto-resistance for room temperature and liquid-nitrogen temperature. No detectable effect was found.

## Discussion of the Results

### (a). Paramagnetic Direction

In the low-temperature range, the curve (Fig. 3) appears to be a horizontal line and corresponds to the exhaustion range where, in this case, the conductivity is due to  $n$ -type carriers. With increasing temperature the intrinsic range begins, with the characteristic drop of the Hall coefficient and with a change of its algebraic sign from  $n$  type to  $p$  type. The small value of the Hall coefficient corresponds to a large carrier concentration,  $n = 2 \times 10^{20} \text{ cm}^{-3}$ , obtained from the formula  $R_H = 1/ne$ . The formula used is valid for the case of one-only type of carrier and for a degenerate distribution. Actually the carrier distribution is degenerate, as follows from the formula

$$kT_{\text{deg}} = h^2/2m(3n/8\pi)^{2/3},$$

which gives  $T_{\text{deg}} = 1440^\circ K$ . All the measurements reported here are below  $450^\circ K$ .

In the case of high carrier concentrations the excitation energy of the donor levels has no meaning. This is because the wave functions associated with the "impurities" overlap and form a band of energies which overlaps the conduction band. Therefore it was considered useless to extend the measurements to even lower temperatures.

The reversal of sign of the Hall coefficient occurs at  $165^\circ K$ . This unusual reversal from  $n$  to  $p$  type, accord-

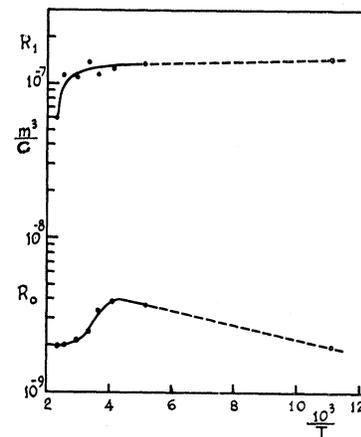


FIG. 5. The two Hall coefficients found from the slopes of the isotherms.

ing to the formula

$$R = - (r/e) (n_e \mu_e^2 - n_h \mu_h^2) / (\mu_e n_e + \mu_h n_h)^2$$

implies that the hole mobility  $\mu_h$  is larger than the electron mobility  $\mu_e$ . By applying the formula  $R_{\text{exh}}/R_{\text{max}} = 4c/(c-1)^2$ , where  $c = \mu_e/\mu_h$ , two values for the ratio of the two mobilities are obtained ( $c = 2.75$ ,  $c = 0.18$ ). Only the one which is smaller than unity is acceptable. Application of the formula  $\mu_e = R_H/\rho$  in the exhaustion range gives the value of the electron mobility  $\mu_e = 130 \text{ cm}^2/\text{Vs}$ . From the already computed ratio of the two mobilities, the value of the hole mobility is determined  $\mu_h = 735 \text{ cm}^2/\text{Vs}$ . Up to now two more crystals are known (CdSb, ZnSb) having higher hole mobility than the electron mobility.<sup>11</sup>

In the measurements of the resistivity the two samples showed different behavior (Fig. 6). In both cases the curve is smooth, without exhibiting any irregularity (sudden drop with increasing temperature) at the reversal temperature, which irregularity is always present in the resistivity curve of samples changing from *p* to *n* type. The values of the resistivity obtained from the two probe pairs differ by 40%, while in the most homogeneous samples this difference is less than 10%. As reported in several papers,<sup>12</sup> the iron sulphides show a large anisotropy of the electrical conductivity (electric field parallel and perpendicular to the *c* axis). It is known that as the sulphur content deviates from the stoichiometric composition, the anisotropy decreases and finally disappears for a composition of  $\text{FeS}_{1.09}$ . In the present material we can say that no important anisotropy of the conductivity is present.

The four voltages of each set are combined by the usual method, and the result is considered to be the Hall voltage ( $U_H$ ). But in reality, the above result includes in addition the Ettingshausen effect which is due to the transverse temperature gradient. Judging from the large carrier concentration, we can assume that the voltage due to the Ettingshausen effect is negligible. This assumption is based on the calculation<sup>13</sup> of the Ettingshausen coefficient for Ge and Si for various temperatures and impurity concentrations. It was found that with increasing impurity concentration, the Ettingshausen coefficient decreases, and also that the effect appears at progressively higher temperatures.

The origin of the large carrier concentration is due to the following contributions: (a) The composition of the crystal deviates somehow from the stoichiometric composition, and this deviation causes the presence of donor levels, and (b) in natural crystals, impurities are always present, of which the nature and concentration

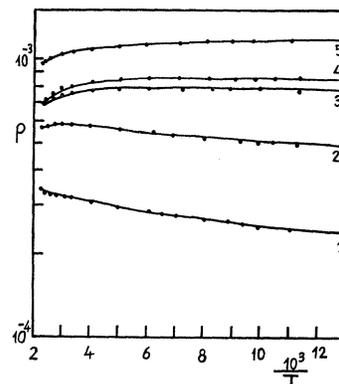


FIG. 6. Resistivity (in  $\Omega \text{ cm}$ ) versus temperature. Curves 1 and 4 belong to samples of case I, curves 2 and 5 case II, and curve 3 case III.

are completely unknown. Usually the carrier concentration obtained in the exhaustion range is assumed to give the donor concentration. The same quantity could be evaluated in a different way by calculating the excess sulfur atoms per unit volume of the material. The value found is  $40 \times 10^{20} \text{ cm}^{-3}$ , which is 20 times larger than the value obtained from Hall data in the exhaustion range.

#### (b). Ferromagnetic Direction

The experiments show that there is no sign reversal of the Hall coefficient (Fig. 5). In Fig. 4 two straight lines are drawn, one through the points in the high-field range and the other through the origin and the first two points. The drawing of the latter section is more or less unsafe because of the lack of measurements in the range 0–200 G.

In the present measurements the slope of the line in the high field section does not provide directly the coefficient  $R_0$  and therefore has to be calculated. The necessity of the correction is due to the fact that the term  $R_s J$  in formula (1) does not become constant in the high field range. Actually if we plot the magnetization curve ( $J \rightarrow H$ ) for a certain temperature, from the thermomagnetic data,<sup>2,14</sup> we see that it consists of a steep original section, terminating at a field of about 1000 Oe, and a gradually increasing section up to the saturation magnetization, which occurs for fields of about 20 000 Oe. In other words this means that in the high-field data of the curve ( $\rho_H \rightarrow B$ ) some contribution is still present owing to the gradual increase of the magnetization. The goal is to make an evaluation of this contribution and draw a corrected line, the slope of which will provide the coefficient  $R_0$ . To carry out the correction we assume that the magnetic data found in the literature<sup>14</sup> are good for our material. To carry out this correction we proceeded in the following way: We converted the magnetization curve ( $J \rightarrow H$ ) to the curve ( $J \rightarrow B$ ) using the formula  $B = \mu_0 H + J$ . Then the correction  $\Delta \rho_H$  for each measured value  $\rho_H$  can be found through the formula  $\rho_H = R_0 B + R_s J$ , which for a fixed value of  $B$  gives  $\Delta \rho_H = R_s \Delta J \simeq R_1 \Delta J$ .

<sup>14</sup> R. Pauthenet, *Compt. Rend.* **234**, 2261 (1952).

<sup>11</sup> L. Pincherle and J. M. Radcliffe, *Advan. Phys.* **5**, 271 (1956).

<sup>12</sup> E. Hirahara and M. Murakami, *Phys. Chem. Solids* **7**, 281 (1958).

<sup>13</sup> H. Mette, W. W. Gartner, and C. Loscoe, *Phys. Rev.* **115**, 537 (1959); **117**, 1491 (1960).

In this way we find the correction  $\Delta\rho_H$  from the known quantity  $\Delta J$ , which denotes the excess magnetization above the level of the end of the original steep section of the curve ( $J \rightarrow H$ ).  $R_1$  is already known from the slope of the original section of the curve ( $\rho_H \rightarrow B$ ). We worked out the correction for those temperatures for which the magnetization curve is available. In the case of Fig. 4 ( $T=197^\circ\text{K}$ ) the corrected line has slope ( $R_0=1.3 \times 10^{-9} \text{ m}^3/\text{C}$ ) which is 34% of the slope of the uncorrected line ( $3.86 \times 10^{-9} \text{ m}^3/\text{C}$ ). In the case  $T=245^\circ\text{K}$  the correction is 36%. As the correction could not be carried out in all the isotherms, because of the lack of magnetic data, the  $R_0$  values shown in Fig. 5 are the uncorrected ones. Of course, the above correction would not be needed if the measurements were extended to fields over 20 000 Oe.

The coefficient  $R_1$  can be found from the slope of the low-field section [method (b)]. For a verification we calculated the same coefficient for the case of  $T=245^\circ\text{K}$  by method (a), using Pauthenet's magnetic data and assuming that the (experimental) high-field section follows the same linear trend up to the saturating field (20 000 Oe). From that point we draw a straight line with slope  $R_0$  (corrected value) that intersects the vertical axis at a point which gives the value  $R_s J_s$ . From this value and the saturation magnetization ( $J_s=80 \text{ emu}=4\pi \cdot 10^{-4} 80 \text{ Vs/m}^2$ ) we find  $R_s$  and then  $R_1$ . The value found in this way was  $R_1=122 \times 10^{-9} \text{ m}^3/\text{C}$ , while method (b) gave  $R_1=132 \times 10^{-9} \text{ m}^3/\text{C}$ .

Difficulty was encountered in determining  $R_0$  and  $R_1$  at the temperature of liquid  $\text{O}_2$  (the given value especially for  $R_1$  is quite uncertain), while it was impossible to find the two coefficients for the temperature of liquid  $\text{N}_2$ . This is owing to unexpected scattering of the experimental points. We did not have occasion to investigate whether the scattering is due to experimental instability or to some type of oscillation. Such oscillatory behavior of the experimental points is visible in Fig. 4, and in general in the data of Table II, but because of the experimental errors the situation is not clear. Our intention is to clarify this point by starting new measurements soon.

Here we might proceed to the following speculation: Measurements of the Hall voltage versus the magnetic field for the paramagnetic case, at room temperature, gave a smooth straight line, passing through the zero point. This gives a well-defined value of the Hall coefficient. On the other hand, in the data for liquid-nitrogen temperature, because of the scattering of the experimental points, the exact form of the low-field section could not be determined, but the extrapolation of the high-field section definitely does not pass through zero, reminding us of the isotherms of the ferromagnetic case. The above experimental events may have some correlation with the shift of the direction of the easy magnetization<sup>14,15</sup> out of the "magnetic plane," which occurs at low temperatures.

<sup>14</sup> K. Adachi, J. Phys. Soc. Japan 16, 2200 (1961).

All the measurements of Table II were performed on the same sample. By x-ray reflection the exact orientation of the sample was determined. Its main face forms an angle of  $7^\circ$  with the crystal plane (110). As reported by Weiss,<sup>16</sup> the direction [100] is the one of easiest magnetization within the magnetic plane. After each series of measurements, the sample was demagnetized.

The usual process for Hall-effect measurements, when applied in ferromagnetic materials, presents an uncertainty if the sample is not demagnetized after each measurement. This is owing to the fact that when we reverse the field, we do not know the exact position of working point on the hysteresis plane. In the present case we assume that the magnetization loop is reduced to a simple magnetization curve.

Hall measurements were continued on two more ferromagnetic samples, of which one has its long axis parallel to the  $c$  axis (case III). The results found were similar to the ones for case II.

Commenting on the influence of temperature, we note from Fig. 5 that the coefficients  $R_0$  and  $R_1$  show parallel variation against temperature. Further, the values of  $R_1$  are practically equal to those of the polycrystalline case. Comparison can be made between the ordinary Hall coefficient  $R_0$  of the ferromagnetic case and the Hall coefficient  $R_H$  of the paramagnetic case, after the sign reversal toward higher temperatures. Both are of the same sign and order of magnitude.

From the value of  $R_0$  for liquid-oxygen temperature, the concentration of carriers (holes) was found as  $80 \times 10^{20} \text{ cm}^{-3}$ . The mobility at that temperature is  $\mu_h=0.7 \text{ cm}^2/\text{Vsec}$ , a value much smaller than that of the paramagnetic sample. One possible reason for the very different behavior of the paramagnetic and ferromagnetic samples might be the magnetic anisotropy and its consequence, the magnetostriction.

Finally a test was done of the Karplus-Luttinger theory,<sup>17</sup> which gives the formula

$$B_1 = A\rho^n$$

relating the two quantities  $R_1$  and  $\rho$ . The formula was applied to the case of that ferromagnetic sample for which all the necessary data are known ( $R_1$  from Fig. 5 and  $\rho$  from Fig. 6, curve 5). Because of the small variation of these quantities (versus temperature), it is difficult to draw a reliable line through the experimental points. However, an attempt was made, which gave  $n=7$ , a value larger than the values for other ferromagnetic materials ( $n$  in the range from 1.4 to 2).

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<sup>16</sup> M. Bin and R. Pauthenet, Compt. Rend. 254, 3078 (1962).

<sup>17</sup> R. Karplus and J. M. Luttinger, Phys. Rev. 95, 1154 (1954).