keep the following in mind: the ZnS(CuCl) crystals, on which we carried out our measurements, are a polytype of a mixed hexagonal-cubic structure, so that, as one finds from measurements of green electroluminescent emission[12] two emitting Z^- states are present, one for each structure, at different energies from the valence band. Furthermore, taking the valence band to be made up of states separated from one another by 0.05 and 0.08 eV, the transitions arising from the two upper levels of the valence band to the Cu^{++} center are clearly visible, and precisely localized, whereas the transition from the continuum to the center does not appear: in fact, although our method allows us to detect $\Delta I/I_0 \simeq 10^{-5}$, when absorption of I_0 is too great, $\Delta I/I_0$ is no longer measurable, even though ΔI is of the same order of magnitude as in the other measurements. This is the case of transitions from the continuum to the Cu^{++} center. From the foregoing one may associate the four broad peaks with transitions from the two levels at the top of the valence band, to the $d(E)$ levels of the two Cu^{++} centers, one present in the cubic and the other in the hexagonal phase. This is reasonable if one takes into account the separation observed between the first pair of peaks and the second pair ($\simeq$0.13 eV), which corresponds to the energy difference one finds between the green emission of the Cu^{++} center in the hexagonal phase and that in the cubic phase ($\simeq$0.125 eV).[12]

Our experimental findings show that the position of the absorption peaks does not vary with applied voltage, whereas the height of the peaks varies linearly with the latter. The possible effect of the field on internal transitions within the center (Stark effect) cannot be detected on our instruments. There is, however, no infrared absorption spectrum shift as a function of applied voltage. The increase in peak height, with no spectrum shift, might show that the number of crystal regions in which the local field has acquired sufficient intensity to excite the centers increases, and in each of these regions the field reaches a value which, for some reason, cannot be surpassed. This may be explained as follows: The applied voltage is such as to increase the barrier field; tunneling increases the number of carriers that travel through the barrier, diminishing its resistance and consequently its potential difference. This mechanism prevents the field from growing beyond a certain value.

ACKNOWLEDGMENTS

The authors wish to thank Professor G. F. Bassani and Dr. E. S. Giuliano for most useful discussions, Professor G. Bonfiglioli for supplying the crystal used in our expreiment, and Dr. P. Perillo for help with the measurements.

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[12] A. Crosnier and G. Curie, *Luminescence of Organic and Inorganic Materials*, edited by H. P. Kallman and G. M. Spruch (John Wiley & Sons, Inc., New York, 1962).

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Hall Effect in CoO, NiO, and α-Fe_2O_3

H. J. van Daal and A. J. Bosman
Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

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The Hall coefficient R_H and resistivity ρ have been measured on ceramic samples of p-type CoO and NiO between 200 and 1500°K and of n-type α-Fe_2O_3 between 960 and 1500°K. Results obtained on single-crystal p-type NiO are also reported. Seebeck-effect data are considered in the discussion of the results. For the paramagnetic phase of NiO and α-Fe_2O_3, the behavior of R_H deviates drastically from that found in the case of a normal-band semiconductor. The sign of R_H is opposite to that normally expected. The corresponding Seebeck effect has the normal sign. R_H remains inversely proportional to the charge-carrier concentration. Furthermore, the Hall mobility ($\mu_H = |R_H|/\rho$) has a value which is smaller than that for the corresponding drift mobility (μ_D). The difference amounts to two orders of magnitude in the case of NiO and to about a factor of 4 in the case of α-Fe_2O_3. Below the Néel temperature, R_H has the normal sign. The anomalous behavior of the Hall effect in the cases of NiO and α-Fe_2O_3 is thought to be due to an interaction between the charge carriers and the magnetization induced in the material by the applied magnetic field. In the case of CoO the behavior of R_H does not seem to be influenced appreciably by the magnetic transition at the Néel temperature. The value of μ_H at high temperatures in the paramagnetic phase is about a factor of 4 lower than that of μ_D. A discussion of the Hall-effect data with regard to the mechanism of electrical conduction in the materials under consideration is also presented.

I. INTRODUCTION

THE mechanism of electrical conduction in transition-metal oxides such as CoO, NiO, and α-Fe_2O_3 has for long been the subject of extensive investigations. According to Verwey and de Boer[1,2] the occurrence of electrical conduction for example in NiO is associated with the presence of Ni ions with different valency at normal lattice sites. This situation can be easily obtained by employing the method of "controlled valency".[3] The introduction of Li into NiO, for instance, results in the formation of (Li^+-Ni^{3+}) acceptor centers.

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[1] E. J. W. Verwey and J. H. de Boer, Rec. Trav. Chim. **55**, 531 (1936).

[2] J. H. de Boer and E. J. W. Verwey, Proc. Phys. Soc. (London) **49**, 59 (1937).

[3] E. J. W. Verwey, *Semiconducting Materials* (Butterworths Scientific Publications, Ltd., London, 1951), pp. 151–161.

Because of thermal excitation, the Ni^{3+} holes can be released from these centers and then move freely through the lattice.[2,3] According to this model the activation energy found in the conductivity is principally determined by the acceptor-ionization energy.

Later, the results of resistivity and Seebeck-effect measurements on NiO and α-Fe_2O_3 led Morin[4] to the different conclusion that the temperature dependence of the conductivity, especially in the case of samples with a relatively small dope, is determined largely by the drift mobility, only a minor contribution being made by the charge-carrier concentration. It was found that the drift mobility increases exponentially with temperature, relevant values of the activation energy lying between 0.1 and 0.7 eV. For the drift mobility at room temperature very low values were found (10^{-8}–10^{-2} cm^2/V sec). Similar conclusions were arrived at by many other authors.[5–10]

According to Heikes *et al.*[5] the activation energy occurring in the mobility is due to polarization of the lattice by the free charge carriers. Conduction is described as a diffusion process wherein a charge carrier jumps from one lattice site to another. This model does indeed lead to a mobility increasing exponentially with temperature. It is known as the thermally activated hopping model.

The apparent nonmeasurability of the Hall effect in these substances was felt at that time to be the logical consequence of an exceptionally low drift mobility. The Hall mobility value of 3×10^{-4} cm^2/V sec for NiO at room temperature obtained at a later data by Fujime *et al.*[11] did fit in with the expectations.

A new era was inaugurated with the investigations on NiO by Zhuze *et al.*[12] and by Ksendzov *et al.*[13] Zhuze measured the Hall coefficient R_H and resistivity ρ on single crystals between 300 and 500°K. The value of the Hall mobility ($\mu_H=R_H/\rho$) at room temperature was 0.2 cm^2/V sec. A lower value (0.07 cm^2/V sec) was found for ceramic samples. The temperature dependence of R_H was found to be almost the same as that of ρ up to 400°K. The Hall mobility decreased slightly with increasing temperature up to 400°K followed by a sharp decrease. Zhuze concluded that the temperature dependence of ρ is almost entirely due to the charge-carrier concentration. He found his results to be in conflict with the hopping model. The same conclusion was reached by Ksendzov on the basis of results obtained from Hall-effect measurements on ceramic samples between 150 and 500°K and from measurements of ρ and the Seebeck coefficient α between 100 and 500°K. Ksendzov arrived at an average value of 0.01 cm^2/V sec for μ_H at room temperature. Further measurements of the Hall effect in NiO performed by Roilos *et al.*[14] on single crystals and by Bosman *et al.*[15] on ceramic samples resulted in a value of 0.25 cm^2/V sec for μ_H at room temperature, confirming the results obtained by Zhuze on single crystals.

Ksendzov was the first to recognize the importance of impurity conduction in NiO at lower temperatures. Because of the presence of donors (oxygen vacancies) the (Li^+-Ni^{3+}) acceptors are partially compensated, thus making an extra conduction via the acceptor centers possible. The final model, as proposed by Ksendzov for NiO, in which, besides conduction in a narrow band, carrier transport occurs simultaneously via impurity centers, is quite analogous to that employed in the case of broad-band semiconductors. The presence of impurity conduction has been definitely confirmed by the results of resistivity measurements on single crystals of NiO down to 20°K performed by Springthorpe *et al.*[16]

Bosman *et al.*[17] have shown that the introduction of the hopping model in the case of NiO was based on erroneous interpretations of resistivity and Seebeck-effect measurements. They derived their arguments from measurements on samples with a small Li content. If grain-boundary effects are avoided and if the contribution of impurity conduction can be neglected in the temperature region under investigation, the temperature dependence of $\log\rho$ and α prove to be completely the same. This means that there is no coercive reason for introducing the hopping model. Measurements can even be interpreted in terms of narrow-band conduction. The value of the drift mobility (μ_D) at room temperature calculated from these measurements is of the order of 1 cm^2/V sec.

In the light of the recent developments described above, one might expect the Hall effect in p-type NiO to be normal, i.e., $R_H=r/pe$, where p and e are the free-hole concentration and absolute value of the electron charge, respectively, and where r denotes the Hall factor which is of the order of unity and which is independent of temperature. The sharp decrease of μ_H as found by Zhuze *et al.*[12] in NiO above 400°K, however, already pointed to an anomalous behavior of R_H. Therefore, the present authors extended the measurements on NiO towards higher temperatures.[15] In the temperature range 300 to 500°K our results for ceramic

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[4] F. J. Morin, Phys. Rev. **83**, 1005 (1951); **93**, 1195 (1954); **93**, 1199 (1954); Bell System Tech. J. **37**, 1047 (1958).

[5] R. R. Heikes and W. D. Johnston, J. Chem. Phys. **26**, 582 (1957).

[6] R. R. Heikes, A. A. Maradudin, and R. C. Miller, Ann. Phys. (Paris) **8**, 733 (1963).

[7] S. van Houten, J. Chem. Phys. Solids **17**, 7 (1960).

[8] G. H. Jonker and S. van Houten, *Halbleiterprobleme VI* (Frederick Vieweg und Sohn, Braunschweig, Germany, 1961), p. 118.

[9] M. Nachman, L. N. Cojocarn, and L. V. Ribo, Phys. Status Solidi **8**, 733 (1965).

[10] G. Parravano, J. Chem. Phys. **23**, 5 (1954).

[11] S. Fujime, M. Murakami, and E. Hirahara, J. Phys. Soc. Japan **16**, 183 (1961).

[12] V. P. Zhuze and A. I. Shelykh, Fiz. Tverd. Tela **5**, 1756 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1278 (1963)].

[13] Ya. M. Ksendzov, L. N. Ansel'm, L. L. Vasileva, and V. M. Latysheva, Fiz. Tverd. Tela **5**, 1537 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1116 (1963)].

[14] M. Roilos and P. Nagels, Solid State Commun. **2**, 285 (1964).

[15] A. J. Bosman, H. J. van Daal, and G. F. Knuvers, Phys. Letters **19**, 372 (1965).

[16] A. J. Springthorpe, I. G. Austin, and B. A. Smith, Solid State Commun. **3**, 143 (1965).

[17] A. J. Bosman and C. Crevecoeur, Phys. Rev. **144**, 763 (1966).

material were in agreement with those obtained by Zhuze on single crystals. The sharp decrease of μ_H starting at about 400°K was found to be the prelude to a total disappearance of the Hall effect at 600°K (see Fig. 3 of this paper). At higher temperatures the Hall effect could again be measured up to 1100°K. Above 600°K it proved that the sign of R_H was reversed. Apart from this sign reversal, the value of $\mu_H(=|R_H|/\rho)$ proved to be two orders of magnitude smaller than that of μ_D. The sign reversal of R_H took place at a temperature near the Néel temperature, suggesting a close relationship between this phenomenon and the magnetic structure of the material. NiO is an antiferromagnetic material with a Néel temperature of 520°K.[18–20] The anomaly observed occurred only in the Hall effect whereas neither the resistivity nor the Seebeck effect were found to be influenced by magnetic-ordering effects.

An anomalous decrease of R_H had already been observed in MnTe single crystals at the Néel temperature when the magnetic field was applied perpendicular to the hexagonal c axis.[21] Also a sign reversal was found if the magnetic field had a direction parallel to the c axis. Conduction in the relevant MnTe samples is achieved by holes in a broad valence band in contrast with the case of NiO where it takes place within a narrow band.

We extended the investigations to other transition-metal oxides in order to establish whether the anomaly observed for NiO could be classified as a general phenomenon. The oxides taken into consideration are CoO and α-Fe_2O_3. CoO has the same crystal structure (NaCl) as NiO. It is antiferromagnetic, with a lower Néel temperature (290°K)[22,23] than that of NiO. α-Fe_2O_3 has a dissimilar crystal structure (corundum). It is antiferromagnetic, with a higher Néel temperature (960°K)[24] than NiO. Between 260°K[24,25] and the Néel temperature of α-Fe_2O_3 the antiferromagnetic structure differs slightly from the ideal case resulting in a weakly ferromagnetic behavior of the material in this temperature range.[26] Since the anomalous behavior of the Hall effect in NiO was mainly found above the Néel temperature we were primarily interested in measurements on CoO and α-Fe_2O_3 in the paramagnetic phase.

In this paper the results are presented of resistivity and Hall-effect measurements performed on ceramic p-type NiO and CoO samples between 200 and 1500°K. Furthermore, results will be given of the same type of measurements and of Seebeck-effect measurements performed on n-type ceramic α-Fe_2O_3 samples between 960 and 1500°K.

II. EXPERIMENTAL

A. Preparation of the Samples

The Li-doped NiO samples were prepared by prefiring intimate mixtures of very pure NiO (grade: Johnson-Matthey) and Li_2CO_3 at 700°C in air. After milling the product obtained, it was pressed into pellets and thereafter compressed hydrostatically. The pellets were fired at 1300°C for 24 h in 1 atm of oxygen and then cooled in the furnace. The density of the samples was about 93% of the x-ray density.

CoO was made by decomposition of $CoCO_3$. The latter material was manufactured starting from very pure Co (grade: Johnson-Matthey). The Li-doped CoO samples were prepared by adding Li_2CO_3 to CoO. This mixture was prefired at 700°C in technical nitrogen. Pellets pressed from the product were heated for 24 h at 1300°C in 1 atm of purified nitrogen (10^{-5} atm of oxygen). This oxygen pressure was maintained during cooling in the furnace. Because of the low oxygen pressure the oxidation degree of the samples remains low. Furthermore, the low oxygen pressure prevents the formation of Co_3O_4 at the grain boundaries during cooling. The density of the samples was about 93% of the ideal value.

The iron-oxide samples were doped with Zr or Nb by firing a mixture of α-Fe_2O_3 with ZrO_2 or Nb_2O_5, respectively. Prefiring occurred at 800°C in air. Final firing was carried out for 3 h at 1300°C in oxygen. To avoid oxidation at the grain boundaries during cooling in the furnace, oxygen was replaced by nitrogen at about 900°C. The M series of α-Fe_2O_3 samples was prepared starting from very pure α-Fe_2O_3 (grade: Koch-Light). "Badische Anilin und Soda Fabrik" (BASF) material was used for the B series. In the latter material Ni is present in a rather large concentration ($\simeq$0.05 at.%) as the main impurity, giving rise to acceptors. It could be concluded from resistivity measurements at high temperatures as a function of deliberate dope concentration that extra donors, presumably oxygen vacancies, are present with a concentration of about 0.03 at.%. The advantage of using BASF starting material is that samples of high density are obtained ($\simeq$98%). For the pure material only densities of 90% were obtained.

In the preparation of the ceramic samples described above, high-Ohmic grain-boundary layers can easily arise, their influence becoming noticeable especially at low temperatures. The absence of these layers was ascertained for the cases of CoO and NiO in the way described in Ref. 17.

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[18] E. G. King and A. U. Christensen, J. Am. Ceram. Soc. **80**, 1800 (1958).

[19] V. G. Bhide and G. K. Shenoy, Phys. Rev. **143**, 309 (1966).

[20] The Néel temperature of 640°K arrived at in Ref. 22 is probably too high.

[21] J. D. Wasscher, A. M. J. H. Seuter, and C. Haas, in *Proceedings of the International Conference on Semiconductcr Physics, Paris, 1964* (Dunod Cie., Paris, 1964), p. 1269.

[22] J. R. Singer, Phys. Rev. **104**, 929 (1956).

[23] E. G. King, J. Am. Ceram. Soc. **79**, 2399 (1957).

[24] C. M. Iserentant, G. G. Robbrecht, and R. J. Doclo, Phys. Letters **11**, 14 (1964).

[25] F. J. Morin, Phys. Rev. **78**, 819 (1950).

[26] I. Dzyaloshinski, J. Phys. Chem. Solids **4**, 241 (1958).

B. Measuring Procedure

The samples were in the form of disks about 8 mm in diameter and about 0.2 mm thick. For electrical contacts a platinum-gold paste (Engelhard 8228) was used. The sample holder has already been described elsewhere.[27]

The dc measuring circuit used when the samples had a resistance lower than 1 MΩ has been sketched in Fig. 1. By adjusting the potentiometer R, placed across current electrodes 3 and 4, the current pattern established in the sample (S) between these electrodes and electrode 1 is such that no appreciable potential difference is present across voltage electrodes 2 and 5. The extra voltage across electrodes 2 and 5 induced by a magnetic field perpendicular to the plane of the sample was dc amplified (A: Keithly 150 AR or Cary 31CV) and then recorded (Rec.: Philips PR 2210A/25). For samples with a resistance lower than a few kΩ's, amplifier and recorder were replaced by a micrograph (Kipp BD2). The magnetic field amounted to 30 kG. The Hall coefficient was determined by averaging data obtained by reversing the direction of electrical current and of magnetic field. The main advantage of the current-balance method as described above is that the output terminals of the sample can be connected directly to the entrance of the amplifier.

For samples with a resistance appreciably larger than 1 MΩ the conventional four-probe compensation method was used.

Considerable care should be taken in these measurements to avoid spurious effects. Most important are those effects which are of thermal origin. One of these effects arises either because of an alteration of the furnace position within the magnet gap or because of a change of the heating-wire position with respect to the furnace tube when the magnetic field is applied. In general the temperature gradient at the place of the sample in the furnace then changes, leading to a Seebeck-voltage change across the measuring electrodes. The presence of temperature gradients in the furnace, longitudinal as well as transverse, cannot easily be avoided because of the small space available in the magnet gap. Seebeck voltages in the materials under investigation amount to about 500 μV/°C at high temperatures. Even a change in temperature difference of only 0.01°C across the measuring electrodes results in a potential change of the same order of magnitude as the Hall voltage. This effect can be avoided by rigidly positioning both the furnace in the magnet gap and the heating wire on the furnace tube. In our case the latter aim was realized by laying a platinum wire bifilarly in a groove made in the outside of an alumina tube. The tube was then covered with a layer of an eutectic Ca-Al-silicate mixture,[28] a material which adheres to the alumina after being heated up to 1400°C in air. The absence of this effect can easily be ascertained: With zero current through the sample no voltage may be induced across the measuring electrodes when the magnetic field is reversed. Moreover, a possible residue of this effect is eliminated by the averaging procedure described above.

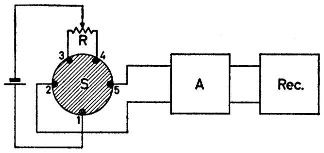

FIG. 1. Principle of the dc circuit used in the measurement of the Hall coefficient.

There is, however, another spurious effect of thermal origin which cannot be eliminated by the averaging procedure. This effect originates from the Lorentz force acting on current leads and sample. Because of these forces the sample can shift and/or rotate somewhat with respect to the holder. A displacement of the sample in the presence of a temperature gradient leads to a pseudo-Hall-effect which, in the measurement in general, is indistinguishable from the real Hall effect. This effect can be suppressed by rigidly positioning the sample on the holder. A check can be made to determine whether the positioning of the sample is rigid enough. For that purpose the current electrodes 3, 1 and 4, 1 (see Fig. 1) have to be short circuited directly at the sample. The real Hall effect is now absent. Lorentz forces on current leads and sample, however, are the same as in the normal measurement, so that the thermal effect remains unchanged, if indeed it is present at all.

The two spurious effects mentioned above can introduce an inertness in the response of the output signal to a change in magnetic field. The corresponding relaxation time is given by the product of heat resistance and capacity of the relevant system. The "magnetic viscosity" found below the Néel temperature[29] in NiO and the "time dependence" as noticed above this temperature[30] can possibly be attributed to the presence of one or both of these effects.

III. RESULTS

A. CoO

In Fig. 2 experimental values for ρ and R_H and corresponding values for μ_H have been plotted as a function of $1/T$ for the case of different p-type CoO samples. The temperature range considered extends

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[27] H. J. van Daal, Philips Res. Repts. Suppl. 3 (1965).

[28] G. H. Jonker, J. T. Klomp, and Th. P. J. Botden, in *Science of Ceramics*, edited by G. H. Stewart (Academic Press Inc., London, 1965), Vol. 2, p. 295.

[29] M. Nachman, F. G. Popescu, and J. Rutter, Phys. Status Solidi **10**, 519 (1965).

[30] I. G. Austin, A. J. Springthorpe, and B. A. Smith, Phys. Letters **21**, 20 (1966). *Note added in proof.* In a recent paper [Proc. Phys. Soc. (London) **90**, 157 (1967)] Austin *et al.* state that their Hall-effect data above T_N were spurious owing to movement of the sample in the magnetic field.

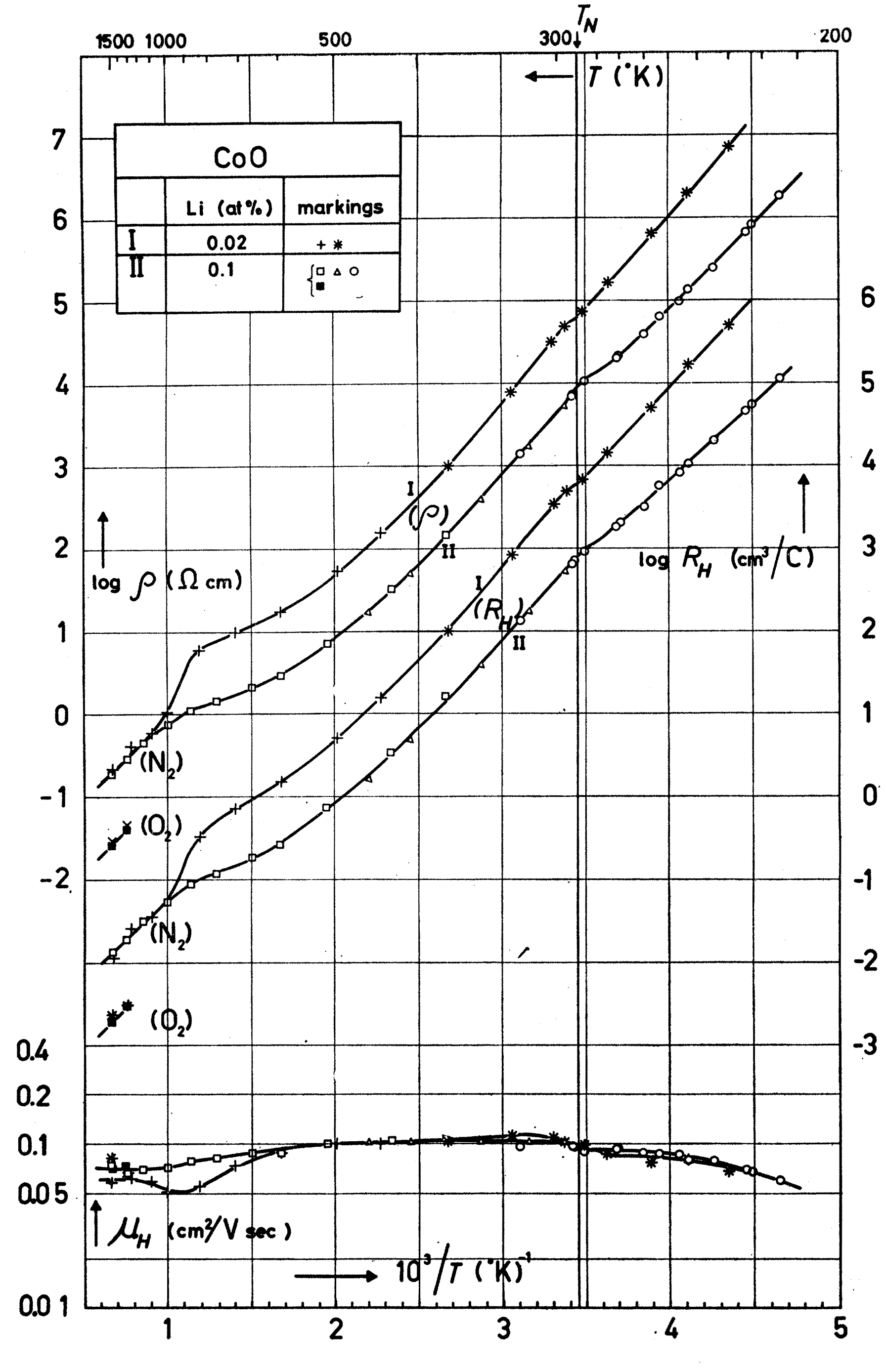

FIG. 2. Resistivity ρ, Hall coefficient R_H, and Hall mobility μ_H as a function of reciprocal temperature for p-type Li-doped ceramic CoO. Measurements have been taken in technical N_2 (10^{-4} atm of O_2). Some data obtained at high temperatures in 1 atm of O_2 are also presented. The Néel temperature T_N has been indicated. Logarithms are to the base 10.

from about 200°K in the antiferromagnetic phase through the Néel temperature (290°K) up to 1500°K in the paramagnetic phase. Measurements were taken in technical nitrogen. At high temperatures some additional data were obtained from experiments in 1 atm of O_2.

R_H has the positive sign and is independent of the magnitude of the magnetic field. Furthermore R_H and ρ have practically the same temperature dependence in the whole range considered leading to an almost constant Hall mobility with a maximum value of 0.1 cm²/V sec. The value of μ_H is practically independent of dope indicating that R_H is inversely proportional to the free hole concentration. At temperatures close to the Néel point a slight change in temperature dependence of R_H, ρ, and μ_H is noticeable. Similar results for ρ have been found by other authors.[14,31] Qualitatively our results are similar to those obtained between 300 and 1000°K by Zhuze *et al.*[32] for non-deliberately-doped single crystals. Zhuze finds a Hall mobility which increases slightly with temperature and which has values between 0.04 and 0.07 cm^2/V sec at 300°K. For a single crystal with a Li content of 1 at.% the value of μ_H between 250 and 400°K as measured by Austin *et al.*[30] increases from 0.01 to 0.02 cm^2/V sec in that temperature range.

Charge-carrier concentration up to 800°K is predominantly determined by thermal release of holes from Li acceptors that become exhausted at higher temperatures. A value of μ_D for holes at high temperatures can be obtained from an extrapolation of ρ from about 800°K towards high temperatures and the assumption $p\simeq[\text{Li}]$. For different samples with Li dopes varying between 0.02 and 3 at.% a value of (0.3 ± 0.1) cm^2/V sec is obtained[33] for μ_D.

Above 800°K a marked decrease of R_H as well as of ρ becomes noticeable especially in the case of the lightest doped sample. At any temperature above 1100°K roughly the same ρ values and the same R_H values are found for the different samples. Values for R_H and ρ obtained in 1 atm of O_2 above 1250°K behave similarly to the corresponding values obtained in N_2, but are one order of magnitude lower. The extra conduction found above 800°K is due to the presence of Co vacancies (V_{Co}).[31]

The Hall mobility starts to decrease slightly at 500°K. For sample II, μ_H reaches a constant value of 0.07 cm^2/V sec between 1000 and 1500°K. For sample I, μ_H first goes through a minimum and then reaches a value of 0.06 cm^2/V sec at high temperatures. The dip found in μ_H at about 900°K for the lightest doped sample is not characteristic of the bulk. At this temperature the concentration of Co vacancies tends to become smaller than that quenched in the material after cooling from 1300°C (see Sec. II A). Because this temperature is relatively low, a diminution of $[V_{\text{Co}}]$ can only be achieved within thin grain-boundary layers. In the case of a sample with a relatively low Li concentration this leads to an increase of grain-boundary resistivity and thus to an increase of the over-all resistivity. R_H is less sensitive to the presence of thin high-Ohmic grain boundaries and remains characteristic of the bulk properties.[34] The data obtained below 500°K certainly will not be influenced by the presence of this type of grain boundary because the Li-acceptor centers which have a lower ionization energy than that of the V_{Co} acceptors then preponderantly determine conduction. At temperatures above 1100°K grain-boundary effects disappear because equilibrium is reached during the measurements throughout the material. At high temperatures no appreciable change is found in the value of μ_H if the concentration of Co vacancies is enlarged due to an increase of oxygen pressure. This confirms that R_H is inversely proportional to the charge-carrier concentration. The value of μ_H at high temperatures amounts to (0.07 ± 0.015) cm^2/V sec, which is significantly lower than the corresponding value of (0.3 ± 0.1) cm^2/V sec found for μ_D. Similar values for μ_D have been derived from gravimetric and resistivity measurements, viz., 0.4 cm^2/V sec at 1350°C [31] and 0.3 cm^2/V sec at 1500°K.[35] The ratio μ_D/μ_H at high temperatures thus lies between 2.4 and 7.3.

B. NiO

In Fig. 3 experimental values for ρ and R_H, and corresponding values for μ_H obtained for different ceramic NiO samples with Li dopes varying between 0.005 and 0.09 at.% are presented as a function of $1/T$. The different values for ρ and R_H found for the two samples with the same Li dope of 0.005 at.% can be attributed to different content of counter-dope elements. Measurements have been taken in 1 atm of O_2. For temperatures between 300 and 1100°K the greater part of the results had already been reported.[15] An extension of data down to 200°K and up to 1500°K is given here. A brief description of the anomalous Hall-effect behavior in the case of NiO can be found in the introduction to this paper.

Nachman *et al.*[29] have reported experimental results up to 700°K. These differ completely from ours. Among other things they find no sign reversal of the Hall effect within the temperature range considered. As far as we can see, however, no precautions seem to have been taken by these authors to avoid the influence of spurious effects. (see Sec. II B.)

Austin *et al.*[30] did find a sign reversal of R_H in the case of single-crystal NiO. However, their outcome points to a lower transition temperature (500°K) than ours (600°K). Furthermore, above the transition temperature they find a value for μ_H one order of magnitude larger than ours. In connection with these results we did some additional measurements on ceramic and also on single-crystalline material around the transition point. Our former findings were confirmed by these measurements. Conduction in the single crystals considered by us (manufactured by Marubeni-Osaka) was predominantly determined by nonstoichiometry, i.e., by the presence of nickel vacancies (V_{Ni}). In Fig. 3 values of ρ as measured in a rapid run on a thick single crystal are given (broken curve). The two steps in which the V_{Ni} acceptors first become singly ionized at lower temperatures then doubly ionized at higher tem-

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[31] B. Fisher and D. S. Tannhauser, J. Chem. Phys. 44, 1663 (1966).

[32] V. P. Zhuze and A. I. Shelykh, Fiz. Tverd. Tela 8, 629 (1966) [English transl.: Soviet Phys.—Solid State 8, 509 (1966)].

[33] A. J. Bosman and C. Crevecoeur (to be published).

[34] J. Volger, Phys. Rev. 79, 1023 (1950).

[35] A. I. Shelykh, K. S. Artemov, and V. E. Shvaiko-Shvaikovskii, Fiz. Tverd. Tela 8, 883 (1966) [English transl.: Soviet Phys.—Solid State 8, 706 (1966)].

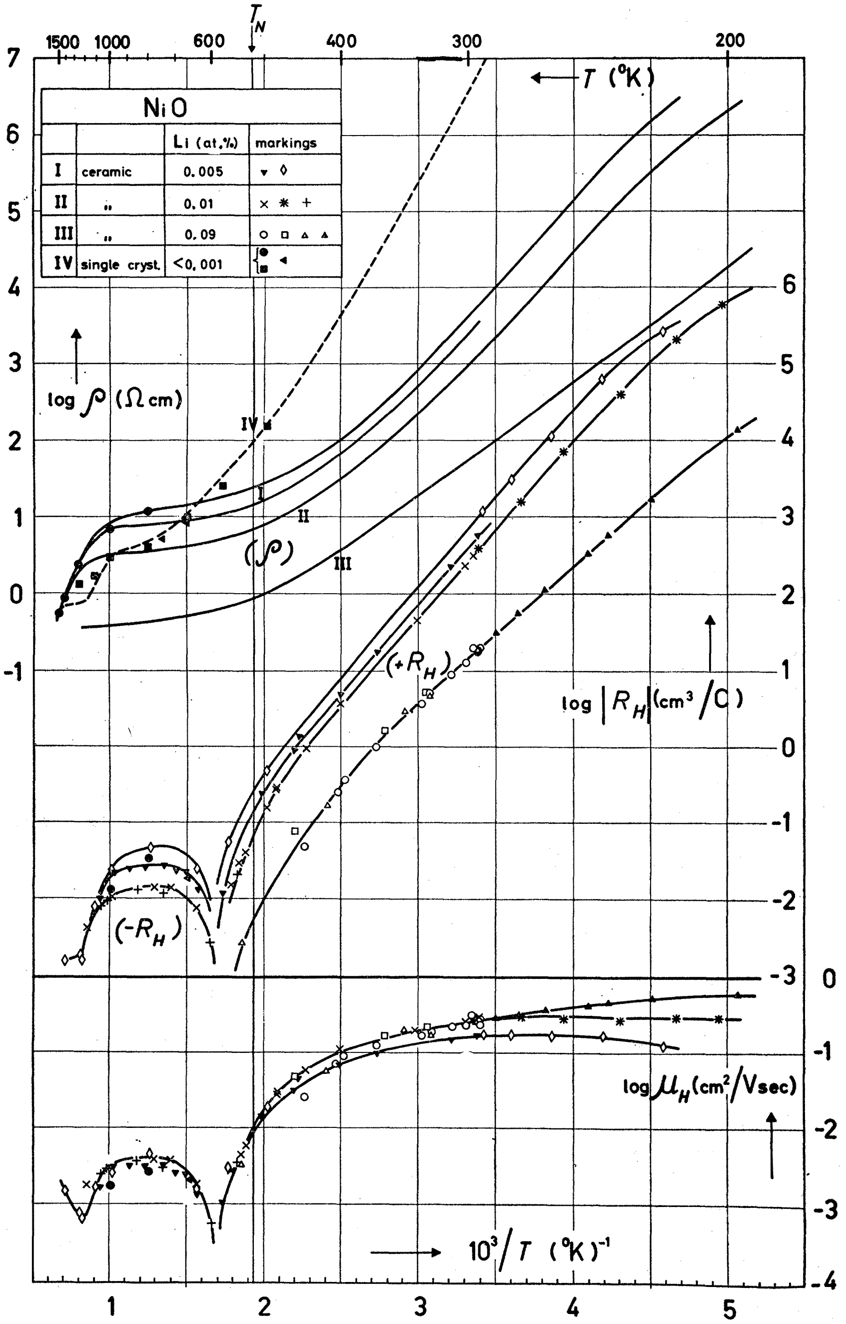

FIG. 3. Resistivity ρ, Hall coefficient R_H, and Hall mobility μ_H for p-type Li-doped ceramic and non-deliberately-doped single-crystal NiO as a function of reciprocal temperature. Values of ρ for ceramic samples have been indicated by solid lines solely. With regard to the resistivity of single crystals at high temperatures, the black circles and squares represent different values for a thin disk (0.4 mm thickness) measured when cooling the sample slowly and rapidly, respectively; the broken line (IV) results from a rapid run of measurements performed on a thick bar ($10\times4\times4$ mm³). The Néel temperature T_N has been marked. Logarithms are to the base 10.

peratures are clearly distinguishable in the temperature dependence of ρ. The resistivity of a thin crystal measured in a rapid run is almost analogous in behavior to that measured on a thick crystal. (See Fig. 3.) However, if the same crystal is cooled down very slowly, as is done in Hall-effect measurements, significantly higher values for ρ are found. (See Fig. 3.) The higher values of ρ for the slowly cooled thin crystal must be attributed to the fact that equilibrium with the gas atmosphere is reached throughout the material down to a lower temperature than that reached in the case of rapid cooling. We were able to obtain some R_H values for thin crystals between 600 and 1000°K. (See Fig. 3.) R_H again proved to have the anomalous negative sign. Corresponding μ_H values were about the same as those resulting for ceramic material. The larger value for μ_H as found by Austin *et al.* is possibly because of the influence of a thermal effect with a negative sign. (See Sec. II B and Ref. 30.) The presence of such an effect also shifts the transition point towards lower temperatures.

In the range 1000–1500°K for the ceramic samples I and II, ρ and R_H decrease markedly with temperature.

Corresponding μ_H values show a minimum at 1200°K. In this temperature range, the influence of nickel vacancies on conduction becomes noticeable for Li-doped material too. These vacancies evidently introduce higher activation energies for conduction than the Li acceptors. Above 1400°K all samples considered show the same ρ behavior which is identical with that already found by Mitoff.[36] The dip found in the values of μ_H as a function of temperature may be due to the same type of grain-boundary effects as proposed for the case of CoO. (See Sec. III A.) These effects can be present in the samples as long as the conductivity due to V_{Ni} centers is higher than that due to Li centers.

In the paramagnetic as well as in the antiferromagnetic phase the value of R_H proved to be independent of the magnetic field. For all samples between 670 and 1000°K, μ_H has a roughly constant value of $(4\pm1)\times10^{-3}$ cm^2/V sec. The drift mobility amounts to $(5\pm2)\times10^{-1}$ cm^2/V sec in the temperature range considered.[17] Thus μ_H is two orders of magnitude smaller than μ_D. It follows from the above that, in spite of the anomalous sign of the Hall effect and its anomalously low value, R_H remains inversely proportional to the charge-carrier concentration.

In the low-temperature range between 200 and 400°K μ_H slowly decreases with increasing temperature for the samples with a Li content of 0.1 at.%. For the lighter doped samples μ_H has lower values and exhibits a maximum at about 300°K. The dissimilar behavior of μ_H for the different samples is probably due to a varying influence of impurity conduction.

C. α-Fe_2O_3

In Fig. 4 values of α, ρ, R_H, and μ_H as measured on various n-type α-Fe_2O_3 samples with different Nb or Zr dopes have been plotted as a function of $1/T$. The temperature range considered lies above the Néel point (960°K) and extends up to 1500°K. In the measuring procedure actually adopted, values for ρ and R_H were measured in 1 atm of O_2 at successively higher temperatures. Thereafter, at the highest temperature, the oxygen pressure was reduced to 0.01 atm, the material allowed to reach equilibrium, and then ρ and R_H values were determined at consecutively lower temperatures. Values of α were determined for these samples only at 1 atm of O_2. For the heaviest doped sample (5) α is constant throughout the whole temperature range. It has the negative sign as might be expected for an n-type sample. For the same sample ρ is almost a constant too. Conduction for this sample is extrinsic with total exhaustion of the donors. For the lighter doped samples the influence of intrinsic conduction becomes noticeable in a decrease of α at high temperatures. The temperature at which this decrease starts is lower according as the dope is lower. For the lightest-doped sample (1) due to intrinsic conduction α even changes sign at the highest temperature. The presence of intrinsic conduction also becomes noticeable, although less markedly so, in a decrease of ρ at higher temperatures. Conduction in all samples is mainly extrinsic at about 1000°K. The increase in the ρ values for the different samples at this temperature is less than inversely proportional to the deliberately added dope. This is because the concentration of oxygen vacancies (V_O) for the lighter doped samples can no longer be neglected. A value for the drift mobility of the electrons of (0.10 ± 0.02) cm^2/V sec has been deduced from the dependence of ρ in the exhaustion range on the

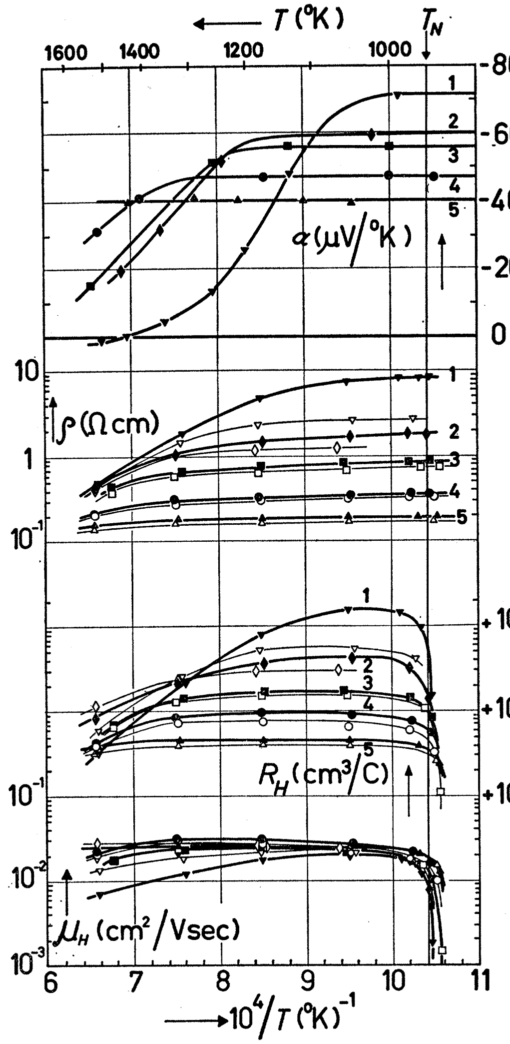

FIG. 4. Seebeck coefficient α, resistivity ρ, Hall coefficient R_H, and Hall mobility μ_H for ceramic n-type α-Fe_2O_3 samples as a function of reciprocal temperature. The samples numbered 1 through 5 have been doped with 0.01 at.% Zr (1), 0.1 at.% Zr (2), 0.12 at.% Nb (3), 0.25 at.% Nb (4), and 1 at.% Zr (5). Samples 1 and 2 belong to the M series, 3-5 to the B series (see Sec. II A). The black markings represent values obtained in 1 atm of O_2, the open markings indicate values resulting from measurements in 0.01 atm partial pressure of O_2. The Néel temperature has been marked T_N.

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[36] S. P. Mitoff, J. Chem. Phys. 35, 882 (1961).

dope and from the assumption that the free-electron concentration equals the effective dope.[37]

The Hall coefficient behaves quite anomalously. For all samples at all temperatures considered in Fig. 4, R_H has the positive sign, i.e., opposite to that of α. At a temperature close to the Néel point, R_H goes through zero and changes sign below this transition temperature. There, in the weakly ferromagnetic range, it depends largely on the spontaneous magnetization as already found before.[4] We were not able to separate the contributions to R_H arising from the spontaneous magnetization and from the external field with magnetic field values up to 30 kOe. The behavior of R_H at temperatures around the Néel point is analogous to that found in the case of NiO. For α-Fe_2O_3 too R_H has the normal sign below the Néel point and the anomalous sign above this temperature. Above the transition temperature in the extrinsic range (between 1000 and 1100°K)μ_H for all samples has about the same value of (0.025 ± 0.005) cm^2/V sec. Thus the value of μ_H is about a factor of 4 smaller than that of μ_D. The dope invariance of μ_H implies that R_H is inversely proportional to the free-electron concentration. Furthermore, R_H proves to be independent of the magnitude of the applied magnetic field. Thus R_H remains proportional to the normal Hall coefficient in spite of the anomalous sign and value of the proportionality constant. The influence of intrinsic conduction on the value of R_H also becomes noticeable at higher temperatures especially in the case of the lighter doped samples when measured in 1 atm of O_2. The decrease of μ_H—e.g., for sample 1 as measured in 1 atm of O_2—is due to this effect. When the oxygen pressure is lowered, it is seen that μ_H again increases at high temperatures. This is because the influence of intrinsic conduction is reduced due to an increase of oxygen-vacancy donors.

IV. DISCUSSION

In Table I a survey is given of the results for CoO, NiO, and α-Fe_2O_3. With regard to the behavior of R_H, a striking difference has been found between NiO and α-Fe_2O_3 on one side and CoO on the other. For p-type NiO, with increasing temperature R_H shows a sign reversal from positive to negative at a temperature somewhat above the Néel point and remains negative up to 1400°K. Prior to this sign reversal a sharp decrease of μ_H sets in already at 400°K. In the case of n-type α-Fe_2O_3, with increasing temperature R_H changes sign from negative to positive at the Néel point and remains positive up to 1500°K. For CoO on the contrary, R_H does not change sign at the Néel temperature. Furthermore, μ_H proves to be influenced only weakly by the magnetic transition and in a way which is not relevant for the present discussion. (See Fig. 2.) These results suggest that for p-type NiO and n-type α-Fe_2O_3 the Hall effect is markedly influenced by the magnetic properties of the material whereas no such influence seems to exist in the case of p-type CoO. The difference found in the case of CoO between the values of μ_H and μ_D at high temperatures may be attributed to the Hall factor r. This factor then lies between 0.15 and 0.40. It is not yet known whether the scattering mechanism for holes in CoO and/or the band structure of this material can lead to such a Hall factor. For all materials, α and ρ remain characteristic of an extrinsic semiconductor up to the highest temperatures considered, the only exception being the lowest doped α-Fe_2O_3 samples.

A transition from extrinsic to intrinsic conduction can lead to a sign reversal of R_H if the charge carriers with a sign opposite to that of the extrinsic charge carriers have a greater mobility. In the case of NiO the sign reversal of R_H takes place at 600°K. No influence from intrinsic conduction could be observed in α up to 1300°K.[17] The same holds for ρ even up to 1300°C. At this temperature, conduction in undoped NiO at oxygen pressures varying between 10^{-4} and 1 atm is still fully determined by the concentration of doubly-ionized Ni vacancies.[36] The behavior of α and ρ is in agreement with the large value of 4 eV for the energy gap of NiO.[38,39] Because of this large value, the intrinsic equilibrium constant $K_i(=pn)$ is extremely small at 600°K. The sign reversal of R_H cannot therefore be attributed to the onset of intrinsic conduction, not even if the ratio between electron mobility (μ_n) and hole mobility (μ_p) were high. Furthermore, the ratio μ_n/μ_p cannot be expected to be very large in the paramagnetic phase because there, owing to spin-disorder scattering, electron mobility is limited to about 1 cm^2/V sec whereas the experimental value for μ_p is 0.5 cm^2/V sec. It has been suggested by Fisher *et al.*[40] that the concentration of free electrons might be significantly enhanced compared to that of free holes because of the presence of native defects with a donor character, thus leading to a sign reversal of R_H. It has, however, been shown by the present authors[41] that this suggestion is based on an erroneous interpretation of the electroneutrality condition. For the case of α-Fe_2O_3, the influence of intrinsic conduction on ρ and α for the heaviest doped sample is negligible up to 1500°K. In this case a positive Hall effect at this temperature could only be explained if μ_p/μ_n has a very large value. This is again quite improbable because of the presence of spin-disorder scattering. Moreover, it can be deduced from the behavior of α and ρ for the lightest doped sample that $\mu_p \lesssim \mu_n$. It is therefore questionable whether R_H can ever change sign for an n-type α-Fe_2O_3 sample due to

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[37] A. J. Bosman (to be published).

[38] R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

[39] Ya. M. Ksendzov and I. A. Drabkin, Fiz. Tverd. Tela. **7**, 1884 (1965) [English transl.: Soviet Phys.—Solid State **7**, 1519 (1965)].

[40] B. Fisher and J. B. Wagner Jr., Phys. Letters **21**, 606 (1966).

[41] H. J. van Daal and A. J. Bosman, Phys. Letters **23**, 525 (1966).

TABLE I. Summary of experimental data for ceramic CoO, NiO, and α-Fe_2O_3 samples. R_H: Hall coefficient; μ_H: Hall mobility; μ_D: drift mobility. The value of γ has been calculated using the relation: $R_H=(1+\gamma)R_{\mathrm{norm}}$, with $R_{\mathrm{norm}}=\pm 1/ne$. AF: antiferromagnetic; WF: weakly ferromagnetic; par: paramagnetic. The temperature ranges in which the mobility values as given are valid can be found in the text.

Material	CoO		NiO		α-Fe_2O_3	
Dope	Li: 0.02–0.1 at.%		Li: 0.005–0.09 at.%		Nb: 0.12–0.25 at.% Zr: 0.01–1	
Conduction type	p-type		p-type		n-type	
Néel temperature	290°K		520°K		960°K	
Magnetic structure	AF	par	AF	par	AF (WF)	par
Sign of R_H	+	+	+	−	−	+
μ_H (cm²/V sec)		0.055–0.085		0.003–0.005		0.02–0.03
μ_D (cm²/V sec)		0.2–0.4		0.3–0.7		0.08–0.12
μ_D/μ_H		2.4–7.3		60–230		2.7–6.0
$-\gamma$				1.005–1.015		1.2–1.4

this effect. For the case of CoO, the value of μ_H at high temperatures remains unchanged when the hole concentration is enlarged by one order of magnitude due to oxidation. This demonstrates that for CoO too the influence of intrinsic conduction is negligible up to the highest temperatures considered.

An anomalous negative sign of R_H was observed for the case of p-type UO_2 single crystals at relatively low temperatures.[42] At higher temperatures a transition to the normal sign takes place. A normal behavior of ρ and α is found at all temperatures. Anomalous effects have also been found for p-type single crystals of Si[43] and InAs.[44] These anomalies can be attributed to the presence of generally very thin n-type surface layers and/or small n-type inclusions. An explanation of the extreme sensitivity of R_H to the presence of thin inversion layers has only been given for the case of InAs where the electron mobility is much higher than the hole mobility.[45] Inversion grain boundaries, if present in the samples investigated by us, might also introduce an anomalous sign of R_H. However, in the case of NiO, identical results have been obtained for ceramic as well as for single-crystal material. This could hardly be expected for samples with such a large difference in surface area if inversion layers played a dominant role. Furthermore, at 1400–1500°K the materials under investigation reach equilibrium with the gas atmosphere within a short period of time. The existence of inversion layers therefore seems hardly possible. Nevertheless, for such an equilibrium state the sign of R_H remained anomalous in the case of NiO and α-Fe_2O_3. Furthermore, an extra reduction of α-Fe_2O_3 might be expected to lead to a complete or partial elimination of p-type surface layers, if present at all. However, for the lighter doped samples the anomalous Hall effect even increased due to this reduction. Therefore one can hardly believe that the anomalies observed are due to the presence of inversion layers.

It may be concluded from the above that in almost all cases considered conduction is achieved in each material by one type of carrier only and that the influence of inversion layers is negligible. It follows then that for the cases of NiO and α-Fe_2O_3 a new mechanism must be introduced in order to explain the experimental results.

The anomalies observed in the paramagnetic phase of NiO and α-Fe_2O_3 occur only in the Hall effect and neither in the resistivity nor in the Seebeck effect. This suggests that the origin of the anomalies lies in the magnetization induced by the magnetic field that is applied when the Hall effect is measured. Evidently this magnetization interferes with the drift current and gives rise to an anomalous Hall effect. A theory of the interference between the magnetization and the drift current has been developed by Maranzana[46] for antiferromagnetic as well as ferromagnetic materials. As already pointed out in his paper, it is questionable whether this theory can be employed in the case of the transition-metal oxides considered. Nevertheless, qualitatively the outcome of Maranzana's theory for an antiferromagnetic semiconductor is in accordance with the experimental results obtained in the cases of NiO and α-Fe_2O_3.

Maranzana considers two different contributions to the Hamiltonian describing the motion of a charge carrier which are of magnetic origin and arise because of disorder in the magnetic-ion lattice. One of these is the well-known interaction between charge-carrier spin and ion spins, that causes spin-disorder scattering and consequently contributes to the resistivity. The other contribution is due to the interaction between the ion spins and the angular momentum of the charge carrier with respect to the ion positions. A transverse Hall current comes about due to the combined presence of the two interactions mentioned. This theory leads for an antiferromagnetic semiconductor to the following

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[42] P. Nagels, Atomic Reactor Centre, Mol. Belgium (private communication).

[43] E. H. Putley and W. H. Mitchell, Proc. Phys. Soc. (London) **72**, 193 (1958).

[44] H. Rupprecht, Z. Naturforsch. **13a**, 1094 (1958).

[45] J. R. Dixon, J. Appl. Phys. **30**, 1412 (1959).

[46] F. E. Maranzana, Phys. Rev. (to be published).

expression for the Hall coefficient:

$$R_H=(1+\gamma)R_{\text{norm}}, \quad (1)$$

where R_{norm} denotes the normal Hall coefficient ($\pm r/ne$) and γ is a term which for a given material depends on temperature only. At low temperatures, where antiferromagnetic ordering is complete, $\gamma=0$. With increasing temperature, starting slightly below the Néel temperature, γ drops below zero and reaches some negative value at this temperature. Above the Néel point γ remains roughly constant up to high temperatures. If $\gamma<-1$ at the Néel temperature, the Hall effect reverses sign in the vicinity of this temperature. From the theory in its present state only values of γ two orders of magnitude smaller than -1 can be obtained.

Qualitatively, Maranzana's theoretical result exhibits the following features found experimentally for R_H in the case of NiO at temperatures below and above T_N and in the case of α-Fe_2O_3 above T_N:

(a) At all temperatures considered R_H is independent of the magnitude of the magnetic field.

(b) R_H at all temperatures remains inversely proportional to the charge-carrier concentration.

(c) The ratio R_H/R_{norm} with increasing temperature drops below unity starting at some temperature below T_N. In the case of NiO this temperature is 400°K.

(d) A sign reversal of R_H might take place at the Néel temperature irrespective whether conduction is achieved by holes (NiO) or by electrons (α-Fe_2O_3). This can be explained by the theory only if indeed $\gamma=-1$ at the Néel temperature.

(e) The sign of R_H remains reversed up to high temperatures, i.e., up to $T\simeq 3T_N$ and $T\simeq 1.5T_N$ for NiO and α-Fe_2O_3, respectively. In the temperature range considered above T_N, γ is indeed roughly temperature-independent.

A value of γ can be derived on the basis of Eq. (1) from the ratio μ_D/μ_H, if only the Hall factor r is known. The values of γ given in Table I have been calculated assuming that $r=1$.

In the case of CoO the magnetic contribution to R_H, i.e., the term γR_{norm}, seems to be absent. If one ascribes the difference between μ_H and μ_D at high temperatures to the presence of the term γR_{norm} this would lead with $r=1$ to $0.6<(-\gamma)<0.9$. In that case one would expect with decreasing temperature a significant increase of μ_H starting at the Néel temperature. This increase, however, has not been found. The absence of the magnetic term is not yet understood. It might be connected with the fact that the Co^{3+} ion in CoO can be diamagnetic, its six $3d$ electrons having the low-spin configuration. On the contrary, in the cases of NiO and α-Fe_2O_3, the Ni^{3+} and Fe^{2+} ion, respectively, are paramagnetic. In the last part of this discussion, however, it will be pointed out that a free hole in CoO most probably corresponds to a high-spin configuration of a Co^{3+} ion.

It might be asked whether the Hall-effect data give additional information about the mechanism of electronic conduction in the materials considered. The question is whether conduction takes place within a narrow band or by thermally activated hopping of small polarons. (See Sec. I.) The drift mobility of small polarons in the high-temperature range, i.e., for $T>\frac{1}{2}\Theta$, where Θ is the Debye temperature, increases with temperature as $(1/T)\exp(-\epsilon/kT)$.[47] For the case of NiO it had already been ascertained from an analysis of experimental data regarding α and ρ that this material does not exhibit the features characteristic of a hopping semiconductor.[17] (See Sec. I.) In the case of CoO, from the results of a similar analysis, μ_D for holes proves to be temperature-independent below 300°K whereas above 300°K data for α and ρ only allow for a slight increase of μ_D up to high temperatures.[33] This result should be taken into account in the above discussion of the Hall-effect measurements for the case of CoO. It suggests that the free Co^{3+} hole corresponds to a Co^{3+} ion which is in the high-spin state. Electron transfer between a Co^{2+}-lattice ion, which is in the high-spin state, and a neighboring Co^{3+} ion in the low-spin state can be expected to be a thermally activated process.[48] This would introduce an activation energy in the drift mobility, which is not found. In contrast with these results, from a combination of gravimetric and electrical measurements it was concluded by Fisher *et al.*[31] that μ_D for holes in oxidized CoO rises exponentially with temperature ($\epsilon=0.3$ eV) in the range 950–1350°C. The interpretation given by these authors of their experimental results, however, seems to be not justified. Moreover, from the same type of measurements between 900 and 1500°K, Shelykh *et al.*[35] conclude to a temperature-independent drift mobility. With respect to α-Fe_2O_3 the constant value of ρ for the heaviest doped samples between 1000 and 1500°K (see Fig. 4) implies that μ_D should be independent of temperature in the range considered. Below 1000°K, μ_D probably does not vary much down to low temperatures.[37] Summarizing, it can be said that certainly for NiO but probably also for CoO and α-Fe_2O_3, data regarding α and ρ do not support the validity of the hopping model for these substances. It is for precisely this reason that in the analysis given in this paper the Hall effect has been assumed to be normal when disregarding influences of magnetic origin.

The theory for the Hall effect of small polarons does not yet seem to be in a definite state. The findings of different authors are contradictory.[49–51] For the tem-

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[47] T. Holstein, Ann. Phys. (N. Y.) **8**, 325 (1959); **8**, 343 (1959).

[48] A. J. Bosman and C. Crevecoeur (to be published).

[49] L. Friedman and T. Holstein, Ann. Phys. (N. Y.) **21**, 494 (1963).

[50] J. Schnakenberg, Z. Physik **185**, 123 (1965).

[51] Yu. A. Firsov, Fiz. Tverd. Tela **5**, 2749 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1566 (1964)].

perature dependence of μ_H in the high-temperature range, dissimilar results have been obtained, viz., an exponential increase with temperature,[49] an almost temperature-independent behavior[50] and an exponential decrease with temperature.[51] However, practically in all cases considered μ_H is predicted to be much larger than μ_D.

The temperature dependence of μ_H for NiO between 300 and 500°K first gave reason to doubt the validity of the hopping model for this material.[12] (See Sec. I.) However, the extension of the measurements up to higher temperatures by the present authors has revealed the presence of an anomalous contribution to the Hall effect which already becomes noticeable at about 400°K. Therefore the Hall-effect data above 400°K cannot be used to discriminate against one of the models for conduction. For NiO at low temperatures, the magnetic contribution to R_H can be expected, according to Maranzana, to be small. This is probably true at temperatures below 400°K. The data obtained for NiO below 400°K militate against the validity of the hopping model: The value of μ_H below 400°K is at most equal to that of μ_D (see Ref. 17) and decreases with increasing temperature. It is even questionable whether this behavior of μ_H can be explained in terms of small polarons. When considering NiO as a narrow-band semiconductor the Hall factor, just as proposed for CoO, may be significantly smaller than unity, leading to a reduction of μ_H with respect to μ_D.

For the case of α-Fe_2O_3 one can hardly expect to gain additional information on the mechanism of conduction in this material from the Hall-effect data in the temperature range under consideration ($T>960$°K).

In the case of CoO the apparent absence of a magnetic contribution to R_H enables one to draw conclusions concerning the mechanism of conduction. The fact that μ_H is practically independent of temperature between 200 and 1500°K supports the same conclusion, drawn from the results of α and ρ measurements, for the behavior of μ_D. Moreover, at high temperatures, the value of μ_H is smaller than that of μ_D. These data for CoO do not support the validity of the hopping model. They even seem to militate against the supposition that CoO would be a small polaron semiconductor.

V. CONCLUSION

In this paper it is suggested that the Hall effect for the antiferromagnetic phase of NiO, at temperatures above 400°K, and for the paramagnetic phase of NiO and α-Fe_2O_3 is strongly influenced by an interaction between the magnetization induced in the materials, and the charge carriers. Following Maranzana, it is proposed that the Hall coefficient for the paramagnetic phase of NiO and α-Fe_2O_3 is composed of two components: One of these is the coefficient normally found in nonmagnetic band semiconductors (normal component), the other is thought to be due to the interaction mentioned above (magnetic component). In the two cases the magnetic component has a sign opposite to that of the normal component. This applies for conduction achieved by holes (NiO) as well as by electrons (α-Fe_2O_3). Furthermore the magnetic component is proportional to the normal component. The proportionality factor depends on material properties and is fairly constant in a wide temperature range. In the cases of NiO and α-Fe_2O_3 the magnetic component overcompensates the normal component by 1 and 25%, respectively, leading to a sign reversal of the total effect and corresponding reduction of its absolute value.The degree of overcompensation has been calculated on the assumption that the Hall factor for the normal component is unity. Below the Néel temperature in the antiferromagnetic phase of NiO and in the weakly ferromagnetic phase of α-Fe_2O_3 the Hall effect has the normal sign. In the antiferromagnetic phase of NiO a reduction of the Hall coefficient due to the presence of the magnetic component becomes noticeable at temperature above 400°K.

In the case of CoO the magnetic component seems to be absent. The Hall factor in the paramagnetic phase at high temperatures is proposed to be about 0.25.

The Hall-effect data obtained for NiO and CoO support the conclusion, reached at from the results of resistivity and Seebeck-effect measurements, that there is no reason to introduce the hopping model.

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