mission coefficient undertaken experimentally as described previously will yield information regarding the actual recombination cross section of an edge-type dislocation. Currently work is underway in this laboratory to produce samples of germanium with controlled densities of dislocations and isolated lineage lines, and to construct measuring apparatus to detect and measure the effects described in this paper. This work will be discussed in a future publication.

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Relation of Magnetic Structure to Electrical Conductivity in NiO and Related Compounds*

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A qualitative theory is presented in an effort to understand the insulating properties of NiO. If one generalizes this theory to include all stoichiometric binary compounds, having a transition element as cation and an element from group V or VI as anion, a rather startling correlation between the magnetic and electric properties is predicted. Ferromagnetic compounds should be good conductors with a positive temperature coefficient of resistivity while antiferromagnets should be insulators with a negative temperature coefficient of resistivity. The available data indicate that this correlation does exist.

I. INTRODUCTION

Nickel oxide has been the subject of much discussion because of its electrical properties. As the Ni ions form an incomplete *d* band, NiO should, by the usual criterion, be a conductor. However, it is found to be an insulator. This same anomaly is also possessed by a number of other materials: CuO, Fe_2O_3, MnO, MnS, MnSe, CoO, to name a few. Verwey and de Boer[1] have attempted to explain this group of materials on a band model by assuming that the potential barrier for electron motion is sufficiently high to prevent conduction. However, Mott[2] points out that if this were the case one would not be justified in using a band approach. Instead Mott treats the problem using a Heitler-London model which requires the presence of mixed valence states for conductivity. He suggests that conductivity might take place by the formation of $Ni^{+}-Ni^{+++}$ ion pairs if enough energy were available to break up these ion pairs or else if enough pairs were formed so that many degenerate positions existed for the Ni^{+} and Ni^{+++} ions. He makes the further tentative suggestion that the lowest energy state will not contain sufficient $Ni^{+}-Ni^{+++}$ ion pairs. Thus, NiO should be, as is the case, an insulator at ordinary temperatures.

The suggestion of Mott that the electrons are too tightly bound to admit conductivity does not seem tenable when one considers the magnetic properties of the crystal. All the aforementioned examples are found to be antiferromagnetic. This antiferromagnetism is presumed to result from the superexchange interaction, which gives rise to configurations of the type $Ni^{+}-Ni^{++}$ rather than $Ni^{+}-Ni^{+++}$ as suggested by Mott, since in this case the electron transfer is actually from O^{--} to Ni^{++} as shown in Sec. III below. However, the essential idea of Mott's argument, that the metal ions must exist in different valence states, is still valid.

II. SUPEREXCHANGE

The dominant magnetic coupling in compounds of stoichiometric composition is thought to be the superexchange.[3] This interaction comes about from the fact that the compounds are strictly polar (i.e., $Ni^{++}O^{=}$) only in the first approximation. (In a perfect ionic compound, the superexchange interaction would be zero.) There are actually "less ionic" configurations present in the ground state in which an electron has been transferred from the anion to the cation (e.g., $Ni^{+}O^{-}$). The magnetic coupling arising from this electron transfer gives rise to ferromagnetism if the cation has less than five electrons in the *d* shell and to antiferromagnetism if five or more electrons are present in the *d* shell. (It should be pointed out that superexchange is strongly dependent upon the angle made by the two cations with the anion as apex. The interaction is strongest when this angle is equal to 180° and weakest at 90°.)[4]

The problem which we must now understand is why a material ferromagnetically coupled by superexchange

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* Work supported in part by Wright Air Development Center, U. S. Air Force.

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

[2] N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949).

[3] H. A. Kramers, Physica **1**, 183 (1934).

[4] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

is a conductor while those coupled antiferromagnetically are insulators.

III. RELATION TO CONDUCTIVITY

The fact that these "less ionic" states are present a fraction of the time leads immediately to a model for conduction requiring no activation energy. One might thus assume that conduction in materials magnetically coupled by superexchange would be metallic (positive temperature coefficient of resistance) in nature. However, at this point one must consider the difference between antiferromagnetic and ferromagnetic superexchange coupling.

Let us consider first the ferromagnetic case (less than half-filled *d* shell) which is represented schematically below. (The ionic state is shown.)

M^{++}	$O^{=}$	M^{++}	$O^{=}$	M^{++}
↑		↑		↑
↑	↑ ↓	↑	↓ ↑	↑

As we have already mentioned, the transition from the ionic configuration to the less ionic one is effected by the movement of an electron from the $O^{=}$ to a neighboring M^{++}. Under the influence of an applied electric field, one of the $O^{=}$ *p* electrons can travel down the line of atoms represented above, the only requirement being that the vacancies be present in the *p* shells of the appropriate $O^{=}$ ions. Furthermore, from a knowledge of superexchange it is known that only the oxygen *p* electrons with spin parallel to that of the metal *d* shells engage in these transitions. Thus, in the schematic diagram only electrons with up spin will take part in conduction. (Transitions involving the electron with down spin are not forbidden but are energetically much less favorable.)

Now let us consider the antiferromagnetic case.

M^{++}	$O^{=}$	M^{++}	$O^{=}$	M^{++}
↑		↓		↑
↑		↓		↑
↑		↓		↑
↑	↓ ↑ 1	↓	↓ ↑	↑
↑		↓		↑
I		II		III

Electron 1 can transfer to atom II. However, even if a vacancy exists in the oxygen ion to the right of II, electron 1 cannot go on to atom III as the Pauli principle would be thereby violated. Thus, conduction by means of the deviation from perfect ionic character is forbidden in an antiferromagnetic lattice at 0°K, except to the extent that metal ion configurations of higher principal quantum number exist.

At a finite temperature reversed spins exist in the otherwise antiferromagnetic lattice. Each such reversal presents a possibility for conduction. Thus, an antiferromagnet should have a negative temperature coefficient of resistivity.

TABLE I Magnetic and electrical properties of binary compounds

	Substance	—cm (room temp.)	Temperature coefficient of resistivity
Ferromagnetic	MnBi[a]	10^{-4}	positive
	MnAs[a]	10^{-3}	positive
	MnSb[a]	10^{-3}	positive
	CrTe[b]	10^{-4}	positive
Antiferromagnetic	MnO[c]	10^{9}	negative
	FeO[c]	10^{8}	negative
	CoO[c]	10^{8}	negative
	NiO[c]	10^{8}	negative
	CuO[c]	10^{10}	negative
	Fe_2O_3[c]	10^{10}	negative
	MnS[d]	10^{5}	negative
	MnSe[d]	10^{5}	negative
	MnTe[d]	10^{2}	negative

[a] R. R. Heikes (to be published).

[b] Fakidov, Grazhdankina, and Kikoin, Doklady Akad. Nauk. (S.S.S.R.) **68**, 491 (1949).

[c] See reference 1.

[d] C. F. Squire, Phys. Rev. **56**, 960 (1943).

IV. NiO AND OTHER ANTIFERROMAGNETS

Let us now see how NiO can be understood from the foregoing analysis. Remembering that superexchange is only appreciable when the metal ion-oxygen-metal ion angle is 180°, we can think of the Ni ions in NiO as a face-centered cubic lattice made up of four essentially noninteracting simple cubic lattices, each antiferromagnetic within itself. On this basis, each Ni ion interacts with six Ni ions (next nearest neighbors in the actual crystal) all of opposite spin orientation. Thus, NiO should be nonconducting.

It should be noted that although a Ni ion has no neighbors of parallel spin at 180°, there are some at 90°. The present model requires this superexchange coupling to be negligible. From the present theory of superexchange it is clear that the 90° coupling will be small; however, it is not clear that it will be negligible.

A possible objection to the present model may be mentioned here. One might expect that at T_c large anomalies in conductivity would be found and that above T_c conductivity should be large. At present there are not sufficient data on this subject. However, it is worth mentioning that the above effects probably will not occur in most antiferromagnetics because of the pronounced short range order which exists even up to 2 and $3T_c$. Such short range order on the present model would be sufficient to hinder conductivity.

Table I cites the resistance and its temperature dependence for all antiferromagnetic compounds on which data are available. (Resistivities are given only to an order of magnitude.) It should be noted that all have a high resistivity and a negative temperature coefficient as is expected.[5]

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[5] MnTe, which has a somewhat anomalous temperature dependence of the resistivity will be discussed in a succeeding paper.

V. FERROMAGNETIC MATERIALS

Table I also lists the resistivities of the ferromagnetic stoichiometric compounds. It is to be noted that these substances have resistivities 5 to 14 orders of magnitude lower. In addition, the conduction is metallic in sign. In order to see that the order of magnitude of the resistivity is correct, let us make a calculation on a simple model. Considering (see Zener's[6] double exchange) conductivity to be a diffusion process, Zener showed that one could write the following relation:

$$\sigma = Ne^2a^2J/kTh,$$

where N is the number of electrons per unit volume participating in the diffusion process (e.g., equal to the number of Ni^+ ions in NiO), a is the lattice constant, and J is the integral representing the transition of an electron from the anion to the cation. Taking Van Vleck's[7] estimate of 10^3 cm^{-1} for J and assuming that $N \simeq 0.1 \times$number of anions, one finds $10^3\Omega^{-1}$ cm^{-1}. This is the correct order of magnitude for the ferromagnetic materials.

SUMMARY

The present model treats NiO on an atomic basis, the lack of conduction arising from the action of the Pauli exclusion principle. This treatment should be valid as long as cation states of principle quantum number greater than three can be neglected.

The data in Table I show that the predicted qualitative correlation between the magnetic and electric properties is borne out.

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[6] C. Zener, Phys. Rev. **82**, 403 (1951).

[7] J. H. Van Vleck, Grenoble Conference 114 (1951).

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Avalanche Breakdown in Germanium

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It is shown that all germanium junctions studied break down as the result of the same avalanche process found in silicon. An empirical expression for the multiplication inherent in this breakdown process is given for step junctions. Ionization rates for holes and electrons in Ge are derived with the use of this expression. The ionization rate for holes is larger than that for electrons by about a factor of two. The agreement between these ionization rates as a function of field and the theory of Wolff is excellent. It is determined that the threshold for electron-hole pair production is about 1.50 ev and the mean free path for electron (or hole)-phonon collisions is about 130 A.

INTRODUCTION

When *pn* junctions are reverse-biased to sufficiently high voltage, a breakdown occurs and large currents begin to flow. The principal theories for this breakdown depend on internal field emission or a solid state analogue of the Townsend β avalanche breakdown in gases.[1,2] The former mechanism was first proposed by Zener[3] for dielectric breakdown. It involves the direct excitation of electrons from the valence to the conduction bands in high electric fields. In the latter mechanism, electrons or holes in high fields interact with valence electrons to produce electron-hole pairs. An important difference between the two mechanisms is that in the latter case multiplication of charge injected into the junction takes place at voltages below the breakdown voltage. In fact, breakdown is defined as the point at which this multiplication becomes very large. The Zener theory has no such multiplicative effects associated with it.

Recently, McKay and McAfee[1] have demonstrated that charge multiplication takes place in some germanium and silicon junctions at prebreakdown voltages. McKay[2] has found that all silicon junctions in the range studied have multiplicative breakdowns. Breakdowns possibly attributable to internal field emission have been reported in some narrow germanium junctions.[4]

The measurements described in this paper were undertaken to understand the breakdown mechanism in germanium junctions. However, the analysis developed should be applicable to other semiconductors. As a result of the measurements, there is strong evidence that the breakdown process in germanium is the avalanche process and that internal field emission has not been observed. It has also been possible to differentiate between the roles of holes and electrons in the avalanche breakdown process by an extension of the Townsend β theory and to compare the ionization rates obtained with the recent theory of Wolff.[5]

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[1] K. G. McKay and K. B. McAfee, Phys. Rev. **91**, 1079 (1953).

[2] K. G. McKay, Phys. Rev. **94**, 877 (1954).

[3] C. Zener, Proc. Roy. Soc. (London) **145**, 523 (1934).

[4] McAfee, Ryder, Shockley, and Sparks, Phys. Rev. **83**, 650 (1951).

[5] P. A. Wolff, Phys. Rev. **95**, 1415 (1954).