versations and Professors H. A. Bethe and J. G. Kirkwood for several helpful discussions.

APPENDIX.

TABLE OF FOURIER TRANSFORMS IN THREE-DIMENSIONAL SPACE

$F(r)$	$G(h)$	
$F(r)$	$\int F(r) \exp(2\pi i\, \mathbf{h}\cdot\mathbf{r})dr$	(1)
$\int G(\mathbf{h}) \exp(-2\pi i \mathbf{h}\cdot\mathbf{r})d\mathbf{h}$	$G(\mathbf{h})$	(2)
$\delta(r)$	1	(3)
1	$\delta(\mathbf{h})$	(4)
$1/r^2$	π/h	(5)
$\exp(-\pi\alpha^2 r^2)$	$\alpha^{-3}\exp(-\pi h^2/\alpha^2)$	(6)
$[1-\exp(-\pi\beta^2 r^2)]/\pi r^2$	$(1/h)\phi(\pi^{\frac{1}{2}}h/\beta)$	(7)
$1-w(r)$	$1-\sigma(\mathbf{h})$	(8)

$$\phi(x) = 2\pi^{-\frac{1}{2}}\int_x^{\infty} \exp(-t^2)dt$$

Interaction between the d-Shells in the Transition Metals.
II. Ferromagnetic Compounds of Manganese with Perovskite Structure

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Recently, Jonker and Van Santen have found an empirical correlation between electrical conduction and ferromagnetism in certain compounds of manganese with perovskite structure. This observed correlation is herein interpreted in terms of those principles governing the interaction of the d-shells of the transition metals which were enunciated in the first paper of this series. Both electrical conduction and ferromagnetic coupling in these compounds are found to arise from a double exchange process, and a quantitative relation is developed between electrical conductivity and the ferromagnetic Curie temperature.

I. INTRODUCTION

IN a recent paper,[1] the author has interpreted ferromagnetism as arising from the indirect coupling of incomplete d-shells via the conducting electrons. According to the viewpoint therein adopted, all unpaired electrons within each atom or ion strive to attain the configuration of lowest energy, in which, according to Hund's rule, all spins are parallel to one another. Since the conduction electrons carry along their own spins unchanged as they wander from atom to atom, they are able to move within an environment of parallel spins only if the spins of all the incomplete d-shells are pointing in the same direction. This indirect coupling via the conduction electrons will therefore lower the energy of the system when the spins of the d-shells are all parallel. In that paper it was further assumed that the direct coupling between incomplete d-shells always tends to align their spins in an antiparallel manner. It was thereby predicted that ferromagnetism would never occur in the absence of conduction electrons or of some other indirect coupling. As an example of the dependence of ferromagnetism on conduction electrons, the author mentioned the difference in the behavior of manganese atoms in the Heusler alloys and in $MnFl_2$. In both substances the Mn atoms are at least 40 percent further apart than in metallic manganese. The Heusler alloys are both conducting and ferromagnetic, while

$MnFl_2$ is nonconducting and antiferromagnetic. An even more striking correlation between conductivity and ferromagnetism may be found in the recent work of Jonker and Van Santen[2,3] on compounds of manganese with a perovskite structure. It is the purpose of the present paper to discuss this correlation. After a brief review of the experimental data (Sec. II), a theory (Sec. III) is developed of the conductivity and ferromagnetism of these compounds. Here conductivity and ferromagnetism are found to be so closely connected that a relation [Eq. (9)] is established between the electrical conductivity, σ, and the Curie temperature, T_C.

II. REVIEW OF EXPERIMENTAL DATA

The perovskite structure is illustrated in Fig. 1. Small metal ions, in our case manganese ions, form a simple cubic lattice. Oxygen ions are at the centers of the cube edges. Large metal ions, such as La, Sr, Ca, Ba are at the center of each unit cube.

The compounds studied by Jonker and Van Santen[2,3] have the composition $(La_{1-x}A_x)MnO_3$, where A represents Ca, Sr, or Ba. Compounds having the extreme values $x=0$, 1 were neither ferromagnetic nor good electrical conductors, being in fact semiconductors. Only compounds with intermediate values of x were ferromagnetic, the strongest ferromagnetism occurring

[1] C. Zener, Phys. Rev. **81**, 440 (1951).
[2] G. H. Jonker and J. H. Van Santen, Physica **16**, 337 (1950).
[3] J. H. Van Santen and G. H. Jonker, Physica **16**, 599 (1950).

O   : OXYGEN ION
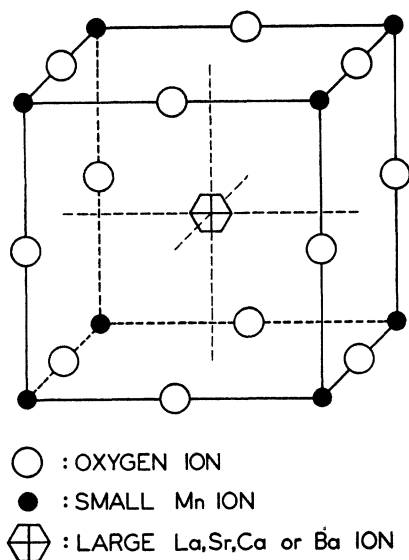
●   : SMALL Mn ION

⊕   : LARGE La,Sr,Ca or Ba ION

FIG. 1. Structure of manganese compounds with perovskite lattice.

in the range $0.2 < x < 0.4$. Only within this same range was the electrical conductivity good, the conductivity at 100°K decreasing by a factor of 0.01 as x decreased to 0.1 or increased to 0.6.

From a study of their observations Jonker and Van Santen concluded that the avidity of oxygen atoms for two electrons is sufficiently great to insure that each oxygen atom in the manganese compounds becomes doubly charged, regardless of the nature of atom A and of the value of the parameter x. In the compound of the extreme composition $LaMnO_3$, each metal atom must then become triply charged, the resulting ionic composition being $La^{3+}Mn^{3+}O_2{}^{2-}$. When, however, one replaces some of the La atoms by atoms having only two electrons outside a closed shell, as Ca, Sr, or Ba, a corresponding number of Mn atoms must become quadruply charged. In support of their viewpoint, Jonker and Van Santen presented the convincing evidence that in the optimum concentration range $0.2 < x < 0.4$, the saturation value of magnetization, extrapolated to 0°K, corresponds precisely to all the unpaired electrons in the manganese ions having spins pointing in the same direction; Mn^{3+} having 4, Mn^{4+} having 3 Bohr magnetons. They attributed the good electrical conductivity within the range $0.2 < x < 0.4$ to the transfer of electrons from Mn^{3+} to Mn^{4+} ions.

III. THEORY

The semiconducting property of pure $LaMnO_3$, and of this compound when small amounts, up to 10 percent, of Ca, Sr, or Ba are substituted for La, suggests the inappropriateness of describing the electronic states in terms of the customary band representation. The alternative description is in terms of localized atomic orbitals. The absence of conductivity of $LaMnO_3$ at low temperatures is obtained simply by requiring that

each Mn ion have a charge of $3+$. The semiconductivity at elevated temperatures then occurs by the thermal ionization of some of the Mn^{3+} ions.

When some of the La^{3+} ions are replaced by, say, Ca^{2+} ions, it is necessary that a corresponding number of Mn^{3+} ions be replaced by Mn^{4+} ions. As suggested by Jonker and Van Santen, it is the migration of these Mn^{4+} ions, accomplished by a Mn^{4+} ion capturing an electron from a neighboring Mn^{3+} ion, that gives rise to electrical conductivity. The precise mechanism whereby such an electron transfer takes place is not trivial, however, since the Mn^{3+} ions are sufficiently far apart as to have no appreciable overlapping. A detailed examination of this mechanism is of value, since we thereby obtain a clue to the relation between electrical .conductivity and ferromagnetism.

We first investigate the simpler problem of the transfer of an electron from a Na atom through a closed shell, e.g., through Cl^-, to an adjacent Na^+ ion. The two Na nuclei will be considered sufficiently far apart so that this transfer would not have occurred at an appreciable rate without an intervening Cl^- ion. Towards this end we denote, by ψ_1 and ψ_2, the wave functions representing the configuration of the system before and after the electron transfer as follows:

$$\begin{array}{ll} \psi_1: & Na\ Cl^-Na^+, \\ \psi_2: & Na^+Cl^-Na \\ & A\quad B\quad C. \end{array} \qquad (1)$$

Since ψ_1 and ψ_2 are degenerate functions, more exact wave functions will be obtained by taking the linear combinations

$$\psi_+ = \psi_1 + \psi_2, \quad \psi_- = \psi_1 - \psi_2. \qquad (2)$$

We denote the energy difference of these two linear combinations by 2ϵ. If, initially, we locate the Na valence electron on one nucleus, this valence electron will thereafter oscillate between the two Na nuclei with the frequency

$$\nu = 2\epsilon/h. \qquad (3)$$

The exchange energy ϵ is given explicitly by the integral

$$\int \psi_1{}^*(H - \epsilon_0)\psi_2 d\tau, \qquad (4)$$

where H is the hamiltonian of the whole system, ϵ_0 is the energy associated with the initial states ψ_1 and ψ_2, and the integral extends over the coordinates and spins of all the electrons. The dominant term in the integrand involves the following product of wave functions:

$$(A|1)^*(B|1)(B|2)^*(C|2). \qquad (5)$$

Here $(A|\ )$, $(C|\ )$ are the wave functions of the valence electron on the left and right Na nucleus, respectively, while $(B|\ )$ is that $3p$ wave function of the Cl^- ion which has a zero angular momentum about the common axis. The form of (5) suggests that we visualize the

electron transfer from one Na^+ ion to the adjacent Na^+ ion as the transfer of an electron from the left Na atom to the central Cl^- ion simultaneously with the transfer of an electron from the central Cl^- ion to the right Na^+ ion. Such a transfer we shall call a *double exchange*.

A slight complication arises when we now return to our original problem of two Mn ions separated by an O^{2-} ion. In compliance with Hund's rule, we shall suppose that each Mn ion is in its configuration of highest multiplicity. If we then define ψ_1 and ψ_2 as follows, the integral (4) is nonvanishing only if the spins of the two d-shells are parallel.

$$\begin{aligned} \psi_1: \quad & Mn^{3+}O^{2-}Mn^{4+}, \\ \psi_2: \quad & Mn^{4+}O^{2-}Mn^{3+}. \end{aligned} \tag{6}$$

The lowest energy of our system thus corresponds to a parallel alignment of the spins of the two transition metal ions. This indirect coupling through the oxygen ion by means of a double exchange should not be confused with the indirect coupling introduced by Kramers,[4] and now called "superexchange." In our case, the system is inherently degenerate owing to the presence of Mn ions of two charges. The double exchange thereby introduced leads to a ferromagnetic alignment of spins. In Kramers' case only excited states are degenerate. The superexchange via these excited states leads to an antiferromagnetic alignment of spins.

We have now already encountered one relation between electrical conductivity and magnetism. Namely, we have seen that the lining up of the spins of adjacent incomplete d-shells of the Mn ions will be accompanied by an increase in the rate of migration of the Mn^{4+} ions, and hence by an increase in the electrical conductivity. The experiments of Van Santen and Jonker[3] do indeed show a marked increase in conductivity just in that narrow temperature interval in which spontaneous magnetization sets in.

We shall now demonstrate that the mechanism which leads to electrical conduction also insures a coupling which leads to ferromagnetism. Let ψ_1 and ψ_2 be defined by (6). We have then seen that the double exchange represented by the integral (4) is the mechanism for electrical conductivity. We have seen further that this double exchange between a Mn^{3+} and a Mn^{4+} ion occurs only when the spins of their respective

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[4] H. A. Kramers, Physica 1, 191 (1934).

d-shells point in the same direction. Now a stationary state is represented neither by ψ_1 nor by ψ_2, but by either of the two linear combinations of (2). Depending upon the sign of the exchange integral (4), the double exchange raises the energy associated with ψ_+, lowers the energy associated with ψ_-, or vice versa. Thus, the energy of one of these two stationary states is lowered by the double exchange which takes place when the d-shell spins are parallel. At low temperatures, regardless of the sign of the exchange integral, the energy of the system will therefore be lowered by a parallel alignment of spins.

It remains to establish a quantitative relation between electrical conductivity and ferromagnetism. On the one hand the magnitude of the exchange energy, ϵ, determines, through Eq. (3), the rate at which an electron jumps from a Mn^{3+} ion across an intervening O^{2-} ion to an adjacent Mn^{4+} ion. The diffusion coefficient for the Mn^{4+} ion is thus given by

$$D = a^2\epsilon/h,$$

where a is the lattice parameter. From the Einstein relation

$$\sigma = ne^2 D/kT$$

between the electrical conductivity, σ, the diffusion coefficient D, and the number of ions (Mn^{4+}) per unit volume n, we obtain

$$\sigma = xe^2\epsilon/ahkT. \tag{7}$$

Here x is that fraction of the Mn ions which have a $4+$ charge. On the other hand, the Curie temperature, T_c, is given approximately by

$$kT_c \cong \epsilon. \tag{8}$$

On elimination of the unknown exchange energy ϵ between Eqs. (7) and (8), we obtain

$$\sigma \cong (xe^2/ah)(T_c/T). \tag{9}$$

This relation agrees excellently with the data of Jonker and Van Santen, differing by not more than a factor of 2 from the observations in the center of the range $0.2 < x < 0.4$ which corresponds to good electrical conductivity and to strong ferromagnetism. In the absence of more detailed published experimental data, a refinement of the above calculations would hardly be significant.