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ON THE THEORY OF ANTIFERROMAGNETISM

by

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ON THE THEORY OF ANTIFERROMAGNETISM*

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ABSTRACT - Overhauser's theory of static spin density waves in an interacting electron gas has been applied to the d-band in antiferromagnetic insulators. Overhauser's theory is reformulated using the equation of motion method. By introducing the Wannier representation one is led to three parameters: U , the correlation energy between two electrons on the same ion; b , the transfer integral for electron transfer between nearest neighbour ions and Δ , the gap in the spectrum of excitations. It is shown that, if Δ is much larger than the d-band width, one obtains a description of the conventional antiferromagnetic insulators, like NiO, as well as of the oxides of vanadium and titanium, which undergo a thermal transition from an antiferromagnetic insulating state to a non-magnetic metallic state. Special attention is paid to this magnetic-to-metallic transition. By calculating the current density and the real dielectric constant, using second order perturbation theory, it is shown that the SDW state represents an insulating state below a critical temperature T_c . Above T_c the state is metallic or remains insulating depending on whether Δ is of the order of U , or small compared to U . Further the critical temperature, the spin susceptibility and the electrical conductivity have been calculated. For reasonable values of the parameters satisfactory agreement with experimental data, available for titanium sesquioxide, is obtained.

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1. INTRODUCTION

Since the introduction of the Heisenberg-Dirac spin Hamiltonian ^{1,2} into the theory of magnetism in general and the idea of superexchange ³ into the theory of antiferromagnetic insulators in particular, a wealth of literature has appeared on the origin of exchange in magnetic materials. It has been customary to distinguish between metallic and insulating magnetic substances, the latter being considered easier to treat. Further, it is usually assumed that the mechanisms responsible for their magnetic properties are entirely different.

A major advance in the theory of superexchange in insulators was made recently by Anderson. ⁴ He introduced the concept of kinetic exchange, a mechanism completely different from Kramers' original superexchange. This type of exchange occurs in transition-metal salts in which the magnetic ions are separated by diamagnetic groups. According to Anderson one should first solve, at least in principle, the complex problem of the motion of a single d-electron in the diamagnetic lattice, thus eliminating the interaction with the diamagnetic groups. The interaction between the renormalized d-electrons is then treated relatively easily. Using the Wannier representation, he was able to show that in second order perturbation theory the most important contribution to the spin dependent interaction between d-electrons on neighbouring magnetic ions comes from a virtual occupation of ionized states. The two parameters which enter the theory are the transfer integral t and the Coulomb interaction U between two d-electrons on the

same ion. Since d-electron transfer only occurs between neighbours with antiparallel spin, the interaction is antiferromagnetic. Further, since U is usually very much larger than b , a permanent occupation of ionized states is impossible, thus making these transition-metal salts insulating. This fact is verified experimentally. For a further understanding of this theory we refer to the review by Anderson,⁴ where also an account of the earlier rather controversial literature is given.

There exist however a few highly interesting transition-metal salts, namely the oxides of vanadium and titanium, which undergo a thermal transition between a low temperature insulating antiferromagnetic state⁵ and a non-magnetic metallic state. If the transfer integral b becomes comparable with the correlation energy U , the d-electrons will begin to wander freely through the crystal. Thus, at least qualitatively, these oxides are contained in Anderson's theory. This way of looking at the problem is similar to the qualitative considerations of Mott on the insulating magnetic state of transition-metal oxides.⁶ Recently Mott's ideas have been formulated more precisely by Kohn.⁷

A complete quantitative theory of antiferromagnetism should in our opinion describe simultaneously:

- (i) Antiferromagnetism in metals (like Cr).
- (ii) A thermal transition between an antiferromagnetic insulating state and a non-magnetic metallic state (oxides of V and Ti).

- iii) Antiferromagnetism in insulating transition-metal oxides, which remain insulating above the Néel temperature (like NiO).

We attempt in this paper to construct such a theory. For this purpose we use the ideas recently put forward by Overhauser.⁸ We start with a Bloch-band of interacting d-electrons, whose degeneracy for simplicity is neglected. Overhauser proves that in a gas of interacting electrons a static spin density wave (SDW) is more stable than the non-polarized paramagnetic state. A SDW corresponds to a splitting of the band of excitations into two bands separated by an energy gap 2Δ . Subsequently we introduce the Wannier transformation and keep only the correlation U between electrons on the same ion and the transfer integral b between nearest neighbours. The parameters of our theory are now U, b and Δ .

Overhauser himself applied his theory extensively to Cr metal. We show that depending on the relative magnitudes of our three parameters one can cover cases (ii) and (iii) as well. In particular we show that, in case Δ is large compared to the band width, Overhauser's state indeed represents an insulating state, capable of undergoing a thermal transition to a non-magnetic metallic state.

In section 2 Overhauser's theory is reformulated, using the equation of motion method in second quantization notation. We show that in Overhauser's state not only the quantities $n_{k\sigma} = c_{k\sigma}^+ c_{k\sigma}$ and $1 - n_{k\sigma} = c_{k\sigma} c_{k\sigma}^+$ have finite c-number average values

but also the quantity $c_{k+Q\downarrow}^+ c_{k\uparrow}$, where $c_{k\sigma}^+$ is the creation operator for electrons of momentum k and spin σ . Q is the wave number of the SDW. Overhauser's state thus corresponds to a pairing of electrons and holes with opposite spin, with the difference in their momenta fixed and equal to Q .

In a Hartree-Fock approximation the SDW state is lower than the unpolarized state, because the attractive Coulomb interaction between electrons and holes can overcome the repulsive interactions between electrons and between holes.

We continue to write down a reduced Hamiltonian, which turns out to be very similar to the well known BCS reduced Hamiltonian.⁹ From there on all the methods used in the theory of superconductivity can be applied to diagonalize this reduced Hamiltonian. We will, however, not discuss these methods in detail.

Section 3 is concerned with thermal properties, whereas section 4 is devoted to electromagnetic properties. Finally, in section 5 a brief comparison with some experimental data is made.

2. SDW GROUND STATE

We start with a Hamiltonian of a system of interacting Bloch electrons of the form

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_k c_{k\sigma} c_{k\sigma} + \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} \sum_{\sigma\sigma'} \langle k_1 k_2 | V | k_3 k_4 \rangle c_{k_1\sigma}^+ c_{k_2\sigma'}^+ c_{k_3\sigma'} c_{k_4\sigma} \quad (1)$$

where ϵ_k is the Bloch energy and $\langle k_1 k_2 | V | k_3 k_4 \rangle$ are the matrix elements of the interparticle potential. $c_{k\sigma}^+$ and $c_{k\sigma}$ are creation

and destruction operators for electrons in Bloch states $|\kappa\sigma\rangle$. The interaction between different Bloch bands will be neglected.

We now consider the equations of motion for the operators $c_{\mathbf{k}\uparrow}^+$ and $c_{\mathbf{k}+\mathbf{Q}\downarrow}^+$, and linearize these equations by defining the c-numbers

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} \tilde{V}_{\mathbf{k}'\mathbf{k}} c_{\mathbf{k}'\uparrow} c_{\mathbf{k}'+\mathbf{Q}\downarrow} = \sum_{\mathbf{k}'} \tilde{V}_{\mathbf{k}\mathbf{k}'}^Q c_{\mathbf{k}'+\mathbf{Q}\downarrow}^+ c_{\mathbf{k}\uparrow}^+, \quad (2)$$

with

$$\tilde{V}_{\mathbf{k}'\mathbf{k}}^Q = \langle \mathbf{k}+\mathbf{Q}\mathbf{k}' | V | \mathbf{k}\mathbf{k}'+\mathbf{Q} \rangle$$

The result is

$$[\mathcal{H}, c_{\mathbf{k}\uparrow}^+] = \tilde{\epsilon}_{\mathbf{k}} c_{\mathbf{k}\uparrow}^+ - \Delta_{\mathbf{k}} c_{\mathbf{k}+\mathbf{Q}\downarrow}^+ \quad (3a)$$

and

$$[\mathcal{H}, c_{\mathbf{k}+\mathbf{Q}\downarrow}^+] = \tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}} c_{\mathbf{k}+\mathbf{Q}\downarrow}^+ - \Delta_{\mathbf{k}} c_{\mathbf{k}\uparrow}^+. \quad (3b)$$

The renormalized Bloch energies $\tilde{\epsilon}_{\mathbf{k}}$ and $\tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}}$, with $V_{\mathbf{k}\mathbf{k}'} = \langle \mathbf{k}\mathbf{k}' | V | \mathbf{k}\mathbf{k}' \rangle$ and $V_{\mathbf{k}\mathbf{k}'}^Q = \langle \mathbf{k}+\mathbf{Q}\mathbf{k}'+\mathbf{Q} | V | \mathbf{k}+\mathbf{Q}\mathbf{k}'+\mathbf{Q} \rangle$, are

$$\tilde{\epsilon}_{\mathbf{k}} = \epsilon_{\mathbf{k}} - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} n_{\mathbf{k}'\uparrow} \quad (4a)$$

and

$$\tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}} = \epsilon_{\mathbf{k}+\mathbf{Q}} - \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}^Q n_{\mathbf{k}'+\mathbf{Q}\downarrow}, \quad (4b)$$

where $n_{\mathbf{k}\uparrow}$ and $n_{\mathbf{k}+\mathbf{Q}\downarrow}$ are the average values of the operators $c_{\mathbf{k}\uparrow}^+ c_{\mathbf{k}\uparrow}$ and $c_{\mathbf{k}+\mathbf{Q}\downarrow}^+ c_{\mathbf{k}+\mathbf{Q}\downarrow}$ in the ground state. The energies $\omega_{\mathbf{k}}$ of the elementary excitations are determined from the secular equation

$$\begin{vmatrix} \tilde{\epsilon}_{\mathbf{k}} - \omega_{\mathbf{k}} & \Delta_{\mathbf{k}} \\ \Delta_{\mathbf{k}} & \tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}} - \omega_{\mathbf{k}} \end{vmatrix} = 0,$$

which gives

$$\omega_{\mathbf{k}}^{\pm} = \frac{1}{2} \left(\tilde{\epsilon}_{\mathbf{k}} + \tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}} \right) \pm \left[\frac{1}{4} \left(\tilde{\epsilon}_{\mathbf{k}+\mathbf{Q}} - \tilde{\epsilon}_{\mathbf{k}} \right)^2 + \Delta_{\mathbf{k}}^2 \right]^{\frac{1}{2}} \quad (5)$$

Thus the band of excitations is split into two bands separated by an energy gap $2\Delta_k$.

The corresponding quasi-particle operators A_k and B_k are then determined as to satisfy the linearized equations (3a,b), i.e.

$$A_k = v_k c_{k\uparrow}^+ + u_k c_{k+Q\downarrow} \quad (6a)$$

and

$$B_k = -u_k c_{k\uparrow} + v_k c_{k+Q\downarrow}, \quad (6b)$$

where u_k and v_k are real. These quasi-particle operators satisfy fermion commutation rules if $u_k^2 + v_k^2 = 1$, as can easily be verified. Representing u_k and v_k by $\sin \nu_k$ and $\cos \nu_k$ respectively, we find on substituting (6) in (3):

$$\tan 2\nu_k = \frac{2\Delta_k}{\tilde{\epsilon}_{k+Q} - \tilde{\epsilon}_k} \quad (7)$$

The ground state wave function $|\phi_0\rangle$, i.e. the quasi-particle vacuum, is defined by

$$A_k |\phi_0\rangle = B_k |\phi_0\rangle = 0,$$

which leads one to the trial function

$$|\phi_0\rangle = \prod_k A_k |\phi_{\text{vac}}\rangle = \prod_k (v_k c_{k\uparrow}^+ + u_k c_{k+Q\downarrow}) |\phi_{\text{vac}}\rangle \quad (8)$$

Here k runs through all the possible k -values of the first Brillouin zone. By calculating the expectation value of the operator $c_{k+Q\downarrow}^+ c_{k\uparrow}$ in this state and substituting the result in (2), we find the gap equation:

$$\Delta_k = \sum_{k'} \tilde{v}_{kk'}^Q \sin \nu_{k'} \cos \nu_{k'} \quad (9)$$

Here $\tilde{\epsilon}_k$ and $\tilde{\epsilon}_{k+Q}$, which implicitly enter through ν_k , are given by

$$\tilde{\epsilon}_k = \epsilon_k - \sum_{k'} v_{kk'} \cos^2 \nu_{k'} \quad (10a)$$

and

$$\tilde{\epsilon}_{k+Q} = \epsilon_{k+Q} - \sum_{k'} v_{kk'}^Q \sin^2 \nu_{k'}. \quad (10b)$$

In order to calculate the ground state energy, we introduce the reduced Hamiltonian

$$\begin{aligned} \mathcal{H}_{\text{red}} = & \sum_{k\sigma} \epsilon_k c_{k\sigma}^+ c_{k\sigma} - \frac{1}{2} \sum_{k,k',\sigma} V_{kk'} c_{k\sigma}^+ c_{k\sigma} c_{k'\sigma}^+ c_{k'\sigma} \\ & - \sum_{k,k'} \tilde{V}_{kk'}^Q c_{k\uparrow}^+ c_{k+Q\downarrow} c_{k'+Q\downarrow}^+ c_{k'\uparrow} \end{aligned} \quad (11)$$

\mathcal{H}_{red} leads to the same equations of motion as (3a,b), as can easily be seen. The ground state energy \mathcal{E} is then defined by

$\langle \phi_0 | \mathcal{H}_{\text{red}} | \phi_0 \rangle$. We find

$$\begin{aligned} \mathcal{E} = & \sum_k \epsilon_k v_k^2 + \sum_k \epsilon_{k+Q} u_k^2 - \frac{1}{2} \sum_{k,k'} V_{kk'} v_k^2 v_{k'}^2 \\ & - \frac{1}{2} \sum_{k,k'} V_{kk'}^Q u_k^2 u_{k'}^2 - \sum_{k,k'} \tilde{V}_{kk'}^Q u_k v_k u_{k'} v_{k'} \end{aligned} \quad (12)$$

Minimizing \mathcal{E} with respect to v_k and using (7), one obtains again the gap equation (9). Thus (9) really represents the stationarity condition for the state $|\phi_0\rangle$.

Up to now we have really done nothing new. The formulas (5), (7), (9), (10a,b) and (12) were already written down by Overhauser,⁸ who started with electrons moving in a periodic spin dependent potential of periodicity $2\pi/Q$. He then determined this potential self-consistently. Our procedure demonstrates clearly that such a self-consistent spin density wave corresponds to a coupling of electrons and holes with opposite spin and with fixed difference in their momenta. Overhauser shows furthermore that a SDW state is more stable than the normal unpolarized Hartree-Fock state, by comparing the ground state energy \mathcal{E} with the energy of the normal

and is

$$2 \left[\frac{1}{4} \left(\tilde{\epsilon}_{K+Q} - \tilde{\epsilon}_K \right)^2 + \Delta_K^2 \right]^{\frac{1}{2}}$$

The smallest excitation energy for pairs is therefore $2\Delta_K$. Similarly a state $B_{K'}^+, A_{K'}^+ |\phi_0\rangle$, with $K \neq K'$, corresponds to a single particle excitation, the excitation energy being $\omega_{K'}^+ - \omega_K^-$. A typical excited state wave function should therefore be written as

$$|\phi_{\text{exc}}\rangle = \prod_{k'} B_{k'}^+ \prod_{k''} A_{k''}^+ |\phi_0\rangle \quad (15)$$

Free energy.

We further define the distribution functions

$$f_k^- = \langle A_k A_k^+ \rangle \quad \text{and} \quad f_k^+ = \langle B_k^+ B_k \rangle ,$$

in terms of which the total energy E becomes

$$\begin{aligned} E = \langle \mathcal{H}_{\text{red}} \rangle &= \sum_k \epsilon_k \left(u_k^2 f_k^+ + v_k^2 f_k^- \right) + \sum_k \epsilon_{k+Q} \left(v_k^2 f_k^+ + u_k^2 f_k^- \right) \\ &- \frac{1}{2} \sum_{k,k'} v_{kk'} \left(u_k^2 f_k^+ + v_k^2 f_k^- \right) \left(u_{k'}^2 f_{k'}^+ + v_{k'}^2 f_{k'}^- \right) \\ &- \frac{1}{2} \sum_{k,k'} v_{kk'}^Q \left(v_k^2 f_k^+ + u_k^2 f_k^- \right) \left(v_{k'}^2 f_{k'}^+ + u_{k'}^2 f_{k'}^- \right) \\ &- \sum_{k,k'} \tilde{V}_{kk'}^Q u_k v_k \left(f_k^- - f_k^+ \right) \left(f_{k'}^- - f_{k'}^+ \right) u_{k'} v_{k'} \quad (16) \end{aligned}$$

Considering that the elementary excitations are independent fermions, one has immediately for the entropy

$$TS = - k_B T \sum_{k,i} \left[f_k^i \ln f_k^i + (1 - f_k^i) \ln (1 - f_k^i) \right], \quad i = +, - \quad (17)$$

Thermodynamic gap.

By defining

$$\Delta_k^{(T)} = \sum_{k'} \tilde{V}_{kk'}^Q \sin \frac{(T)}{k'} \cos \frac{(T)}{k'} \left(f_{k'}^- - f_{k'}^+ \right), \quad (18)$$

as the thermodynamic gap and subsequently minimizing the energy E with respect to $\frac{(T)}{k}$ one gets

$$\tan 2 \frac{(T)}{k} = \frac{2 \Delta_k^{(T)}}{\tilde{\epsilon}_{k+Q}^{(T)} - \tilde{\epsilon}_k^{(T)}}. \quad (19)$$

Here $\tilde{\epsilon}_k^{(T)}$ and $\tilde{\epsilon}_{k+Q}^{(T)}$ are given by

$$\tilde{\epsilon}_k^{(T)} = \epsilon_k - \sum_{k'} V_{kk'} \left[f_{k'}^- \cos^2 \frac{(T)}{k'} + f_{k'}^+ \sin^2 \frac{(T)}{k'} \right] \quad (20a)$$

and

$$\tilde{\epsilon}_{k+Q}^{(T)} = \epsilon_{k+Q} - \sum_{k'} V_{kk'}^Q \left[f_{k'}^- \sin^2 \frac{(T)}{k'} + f_{k'}^+ \cos^2 \frac{(T)}{k'} \right]. \quad (20b)$$

Further, by minimizing the total free energy with respect to f_k^+ and f_k^- and using (18), (19) and (20) one obtains correctly for the distribution functions

$$f_k^- = \frac{1}{\exp \left[\beta \omega_k^-(T) \right] + 1} \quad (21a)$$

and

$$f_k^+ = \frac{1}{\exp \left[\beta \omega_k^+(T) \right] + 1}, \quad (21b)$$

where now

$$\omega_k^{\pm(T)} = \frac{1}{2} \left[\tilde{\epsilon}_k^{(T)} + \tilde{\epsilon}_{k+Q}^{(T)} \right] \pm \left\{ \frac{1}{4} \left[\tilde{\epsilon}_{k+Q}^{(T)} - \tilde{\epsilon}_k^{(T)} \right]^2 + \left[\Delta_k^{(T)} \right]^2 \right\}^{\frac{1}{2}} \quad (22)$$

Eqs. (18), (19), (20), (21) and (22) determine the self-consistency equation for the thermodynamic gap. By putting in these equations the gap equal to zero, one obtains the equation for the

critical temperature.

All these formulas are in principle applicable to metals (Bloch representation) as well as to insulators (Wannier representation). We will now go over to the Wannier representation. In this way we make connection with antiferromagnetic salts and oxides.

Narrow d-band.

We assume that the band width is small compared to the minimum gap $2\Delta_k$. This means that $|\tilde{\epsilon}_k| < \Delta_k$. Furthermore we introduce the Wannier representation and keep only the interaction between electrons located on the same magnetic ion. This interaction will be denoted by U and is given by

$$U = \int |w(r)|^2 \frac{e^2}{|r-r'|} |w(r')|^2 dr dr', \quad (23)$$

where $w(r)$ is the Wannier function at position r . As a consequence the gap Δ_k will be independent of k . We can now make power series expansions in terms of $|\tilde{\epsilon}_k|/\Delta$. Up to second order in $|\tilde{\epsilon}_k|/\Delta$ we find for the gap equation

$$\left(\frac{2\Delta}{U}\right)^3 + \left(\frac{2\Delta}{U}\right)^2 = -2a\left(\frac{b}{U}\right)^2, \quad (24)$$

where

$$ab^2 = \frac{1}{N} \sum_k \frac{1}{4} (\epsilon_{k+Q} - \epsilon_k)^2. \quad (25)$$

Here b is the transfer integral for electron transfer from one ion to another. We keep only transfer to nearest neighbour and have thus

$$b = \int w^*(r) \mathcal{H}_{kin} w(r-R) dr, \quad (26)$$

where R denotes the position of a nearest neighbour. \mathcal{H}_{kin} is the kinetic energy operator. Further, a is under these conditions given by

$$a = \sum_i \sin^2 \left(\frac{Q \cdot R_i}{2} \right), \quad (27)$$

where the sum goes over nearest neighbours only. In obtaining (24) we have assumed that $\tilde{\epsilon}_k$ is approximately given by ϵ_k . In the rest of this paper we shall put $\tilde{\epsilon}_k = \epsilon_k$.

Similarly one finds the equation for the critical temperature

$$T_c \quad \left(\frac{4k_B T_c}{U} \right)^3 - \left(\frac{4k_B T_c}{U} \right)^2 = -\frac{4}{3} g \left(\frac{b}{U} \right)^2, \quad (28)$$

where

$$gb^2 = \frac{1}{N} \sum_k \left(\epsilon_k^2 + \epsilon_{k+Q}^2 + \epsilon_k \epsilon_{k+Q} \right), \quad (29)$$

Eqs. (24) and (28) are shown in Fig. 1.

From Fig. 1 one sees, first of all, that there is no solution for values of b and U such that $2a(b/U)^2 > 4/27$. Thus for these values it is not possible to maintain a SDW, even at $T=0$. For smaller values of $(b/U)^2$, however, there are two solutions with corresponding transition temperatures. If (b/U) is very small, $k_B T_c$ is approximately given by $b(g/12)^{\frac{1}{2}}$ and $U/4$. In order to obtain an approximate expression for T_c for intermediate values of $(b/U)^2$ in the lower branch of Fig. 1, we represent equation (28) by a straight line going through the points $(0,0)$ and $(4/27, 2/3)$. One obtains for T_c

$$k_B T_c \approx (3/2) g(b^2/U) \quad (30)$$

It should be noted that a formula of this type has already been

obtained by Anderson.⁴

We interpret the lower branch of Fig. 1 as corresponding to an antiferromagnetic transition of the conventional type, such as occurs in NiO. Throughout the transition the electrons remain localized on their respective sites. This is plausible, since the thermal energy per electron is approximately equal to $k_B T_c \approx (3/2) g(b^2/U)$, which is very much smaller than the correlation energy U . On the other hand the upper branch should correspond to a transition of the type occurring in the oxides of V and Ti. Above the transition from the antiferromagnetic state to the unpolarized state the electrons are allowed to wander from one site to another, since now the thermal energy per electron is comparable to the correlation energy U . However it is from the outset not clear that both solutions represent insulating states below the transition temperature. In the next section we shall prove, by directly calculating the conductivity and the real dielectric constant, that this is indeed the case.

Before leaving this section there is still one remark to make. One may wonder, given a certain value of $(b/U)^2$, which of the two solutions the system eventually chooses: the one corresponding to the lower branch or that corresponding to the upper branch. By direct computation of the second derivative of the free energy at $T=0$ with respect to Δ one finds that in the upper branch $\partial^2 F / \partial \Delta^2$ is positive, whereas for the lower branch it is negative. This proves that, at least in our model, the upper solution is more

stable and the lower only stationary. This situation is also reflected by the fact that for the lower branch the gap increases with temperature, whereas for the upper branch it decreases at low temperature as $(U/2)[1 - 2 \exp(-\beta\Delta)]$ and at temperature near T_c as $2(3)^{\frac{1}{2}} (k_B T_c)(1 - T/T_c)^{\frac{1}{2}}$, which can easily be verified from (18). We have here thus also the well known fundamental unsolved problem of the antiferromagnetic ground state. It has been argued that one can circumvent these complications by taking anisotropy into account. In a future investigation we will study the effects of anisotropy in our model.

4. ELECTROMAGNETIC PROPERTIES

Electrical Conductivity

We shall calculate the imaginary part $\sigma''(\omega)$ of the conductivity

$$\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$$

at temperature zero in the SDW state. Here ω is the frequency of the applied electric field. In second order perturbation theory $\sigma''(\omega)$ is given by

$$\sigma''(\omega) = -\frac{e^2}{m} \left[N - \frac{1}{m} \sum_{\alpha} |\langle \alpha | P | 0 \rangle|^2 \left(\frac{1}{E_{\alpha} - E_0 - \hbar\omega} + \frac{1}{E_{\alpha} - E_0 + \hbar\omega} \right) \right], \quad (31)$$

where P is the total momentum in the direction of the applied field, $|0\rangle = |\phi_0\rangle$ and $|\alpha\rangle$ are excited states $|\phi_{exc}\rangle$. The only contribution to the matrix elements comes from excited states of the type $B_k^+ A_k^+ |\phi_0\rangle$, which correspond to an energy of excitation $E_{\alpha} - E_0 = \omega_k^+ - \omega_k^-$. From direct calculation one finds that

$$\lim_{\omega \rightarrow 0} \omega \sigma''(\omega) \approx -\frac{Ne^2}{m} \left(1 - \frac{\gamma}{2\Delta} + \frac{3}{4} \frac{\gamma}{\Delta^3} a b^2 \right) \quad (32)$$

Here

$$\tau = \frac{m}{2N\hbar^2} \sum_k \lambda_k^2 |\nabla_k (\epsilon_{k+Q} - \epsilon_k)|^2 ,$$

with λ_k the cosine of the angle between the applied field and ∇_k . According to Kohn,⁷ an insulating state is defined by

$$\lim_{\omega \rightarrow 0} \omega \sigma''(\omega) = 0 ,$$

which leads us to write (32) as

$$\left(\frac{2\Delta}{\tau}\right)^3 - \left(\frac{2\Delta}{\tau}\right)^2 = -6a \left(\frac{b}{\tau}\right)^2 \quad (33)$$

The quantity τ is approximately the kinetic energy required to form a SDW state. Further in equilibrium one has certainly $\tau < U$. Thus one sees that (33) is compatible with the stationarity condition (24).

These considerations constitute a qualitative proof that the SDW state really represents an insulating state, at least under the restrictive assumptions we have made.

Dielectric constant

An alternative way to proof that the SDW state represents an insulating state goes by calculating the real dielectric constant $\epsilon(\omega, q)$, which in perturbation theory is given by¹¹

$$\frac{1}{\epsilon(\omega, q)} = 1 - \frac{4\pi e^2}{q^2} \sum_{\alpha} |\langle \alpha | \rho_q | 0 \rangle|^2 \left(\frac{1}{E_{\alpha} - E_0 - \hbar\omega} + \frac{1}{E_{\alpha} - E_0 + \hbar\omega} \right) \quad (34)$$

Here the symbols have the same meaning as in the case of the conductivity and

$$\rho_q = \sum_{k, \sigma} c_{k+q\sigma}^+ c_{k\sigma} \int u_{k+q}^*(x) u_k(x) dx = \sum_{k, \sigma} c_{k+q\sigma}^+ c_{k\sigma} I(k, q), \quad (35)$$

where $u_{\mathbf{k}}(\mathbf{x})$ is the periodic part of the Bloch functions. Using the same approximations which led to the conductivity (32), one finds that

$$\frac{1}{\epsilon(0,q)} \approx 1 - \frac{\pi e^2}{\Delta^3 q^2} \sum_{\mathbf{k}} |I(\mathbf{k},q)|^2 \left(x_{\mathbf{k}+q} - x_{\mathbf{k}} \right)^2, \quad (36)$$

where $x_{\mathbf{k}} = (1/2) (\epsilon_{\mathbf{k}+Q} - \epsilon_{\mathbf{k}})$. This result shows that $\epsilon(0,q)$ is finite and proves in a far more rigorous way that the SDW state with our approximations represents an insulating state. We emphasize that in calculating σ'' and $\epsilon(0,q)$ we have neglected Umklapp processes.

Spin susceptibility

We will now consider the magnetization of a SDW state in a homogeneous magnetic field H in the direction Q . For this purpose one has to write down the free energy in the presence of a weak magnetic field. This can easily be done. All the results of sections 2 and 3 remain the same, except that $(1/2) [\tilde{\epsilon}_{\mathbf{k}+Q}^{(T)} - \tilde{\epsilon}_{\mathbf{k}}^{(T)}]$ has to be replaced by $(1/2) [\tilde{\epsilon}_{\mathbf{k}+Q}^{(T)} - \tilde{\epsilon}_{\mathbf{k}}^{(T)}] + \mu H$ everywhere. The magnetization M is defined by

$$M = \mu \sum_{\mathbf{k}} \left(n_{\mathbf{k}\uparrow} - n_{\mathbf{k}+Q\downarrow} \right), \quad (37)$$

which becomes

$$M = \mu \sum_{\mathbf{k}} \cos 2 \quad \frac{(T)}{\mathbf{k}} \left[f_{\mathbf{k}}^- - f_{\mathbf{k}}^+ \right]. \quad (38)$$

Near $T=0$, one finds after some algebra for the susceptibility $\chi(T)$

$$\chi(T) = \frac{M}{H} = \frac{\mu^2 N}{\Delta(T)} \left[1 - 2 \exp(-\beta\Delta) \right] \left\{ 1 - \frac{3}{2} a \left[\frac{b}{\Delta(T)} \right]^2 \right\} \quad (39)$$

In case $\Delta^{(T)}$ remains practically constant with temperature, let us say up to $T = T_1$, (39) still represents a good approximation for $\chi(T)$ up to T_1 .

$$\text{For } T = T_c \text{ one has } \chi(T_c) = \frac{\mu^2 N}{2k_B T_c} \left[1 - \frac{1}{8k_B^2 T_c^2 N} \sum_k (\epsilon_k^2 + \epsilon_{k+Q}^2) \right]. \quad (40)$$

Neglecting completely the transfer integrals, (39) and (40) imply that $\chi(0) = \chi(T_c)$. In case the transfer integrals are not zero, (0) is smaller or larger than $\chi(T_c)$ depending on the particular form of ϵ_k .

It should be emphasized that the formulas (39) and (40) are only valid in the upper branch of Fig. 1. It turns out that such expansions in $|\epsilon_k|/\Delta$ do not converge rapidly in the lower branch. Consequently it would be necessary to solve the gap equation exactly.

5. COMPARISON WITH EXPERIMENT

We will now apply briefly the above developed theory to the case of Ti_2O_3 , where sufficient experimental data are available.

The spin susceptibility of Ti_2O_3 ¹² is approximately constant over a wide range of temperatures and rises rather sharply near the critical temperature. Assuming that in this case $\Delta^{(T)}$ remains approximately constant up to temperatures near T_c , and then drops rather sharply to zero, the behaviour of the susceptibility is qualitatively reflected by (39) and (40). Whether the

susceptibility rises or falls near T_c , depends on the particular form of ϵ_k , which we do not know in the case of Ti_2O_3 . From $T_c = 450^\circ K$ and $\Delta \approx 2k_B T_c$, we find that $\Delta \approx 0.08$ eV and $\chi(0) = N\mu^2/\Delta \approx 2.8 \times 10^{-6}$ cgs/gr. Further $U \approx 2\Delta \approx 0.15$ eV. Here we have tacitly assumed that the transfer integrals do not change the order of magnitude of these values. Experimentally $\chi(0) = 0.8 \times 10^{-6}$ cgs/gr. * The agreement is satisfactory, whereas we also believe that the value for U is reasonable.

The electrical conductivity σ' varies for temperatures below the critical temperature exponentially. We make the hypothesis that one can account for this behaviour by assuming that there are two types of electrons: superelectrons and current carrying normal electrons. The number of superelectrons should vary at low temperatures as $1 - \exp(-\beta\Delta)$. We thus propose that σ' can be represented by

$$\sigma' = \text{Const.} \exp(-\beta\Delta) . \quad (41)$$

Comparison with the experimental curve ¹³ leads to $\Delta \approx 0.1$ eV. Considering the gross nature of such a model, Δ is in good agreement with the gap obtained from the susceptibility. Near T_c , the conductivity drops rather sharply. This fact lends additional support to our assumption that $\Delta^{(T)}$ varies only slightly over a wide range of temperatures. It should be noted that there is a certain similarity with the "two fluid" model of superconductivity. However not too much significance should be attached to this analogy.

* Actually $\chi(T)$ rises sharply for low temperatures, reportedly due to paramagnetic impurities. $\chi(0)$ has been obtained by subtracting this contribution.

6. CONCLUSION

The model which we have presented in the preceding sections is an attempt to put the phenomenon of antiferromagnetism on a more general basis. It is applicable to metals, like Cr; to insulators, like NiO, and in particular to substances undergoing an insulator-metal transition, like Ti_2O_3 . We propose to call substances which show a magnetic-to-metallic transition superantiferromagnets. In the case of insulating antiferromagnets and superantiferromagnets the model starts with a d-band in which the electrons are already hybridized with the diamagnetic groups, separating the magnetic ions. Thus, it is supposed that the crystal field part of the problem has already been treated beforehand. Then a SDW is postulated and determined self-consistently, leading to a gap equation. The parameters of our theory are the correlation, U , between two electrons on the same magnetic ion; the transfer integral, b , for electron transfer from one ion to its nearest neighbours; and the gap Δ . The agreement with experimental data is satisfactory.

The model is of course very approximate in that band interaction, anisotropy effects and correlation between electrons on different ions have been neglected. Although we believe that the influence of these effects is not serious, it would be necessary to prove this.

Finally we like to emphasize that the superantiferromagnets are unique systems to study the properties of a dilute gas of interacting electrons. It would therefore be highly desirable

to search for other superantiferromagnets and to have more experimental data available.

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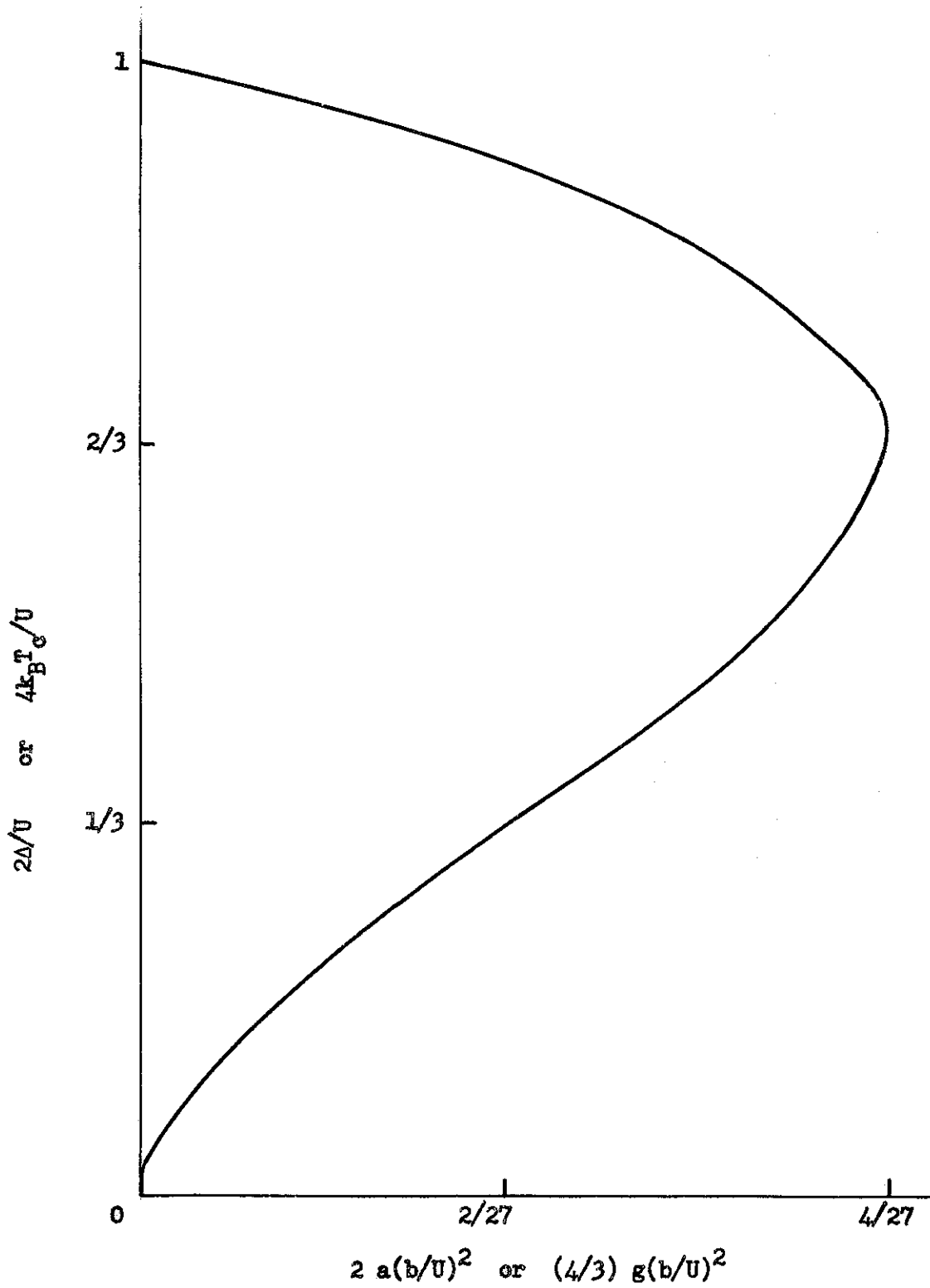


Fig. 1. Stationarity condition for the insulating antiferromagnetic state together with the corresponding critical temperatures.