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[10]Strictly speaking, the reasoning which has lead to Eq. (5) is valid only for states which are eigenstates of the magnetic Hamiltonian alone, while in sodium nitrite there exists evidence of small second-order quadrupole effects, which would mix states of different m. On the other hand an evaluation of the effects associated to the presence of a second-order quadrupole interaction on nuclear relaxation has shown that they can be neglected in our case. Thanks are due to G. Bonera for having brought out this point.
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EXCITONIC PHASES

W. Kohn
Université de Paris, Paris, France, and University of California, San Diego, La Jolla, California
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A number of recent papers[1,2] have discussed a phase which is expected to occur at low temperatures in solids with a small gap, positive (insulators) or negative (semimetals). All previous studies, except for the work of Zittartz, discuss in detail only the simplest case in which the conduction band and the valence band are both taken as spherical. In this case, the new phase is found to be an insulator in the sense that at zero temperature there is a finite excitation energy for charge-carrying excitations. This is, however, an exceptional result. Zittartz,[2] in studying the case of valence and conduction bands of different shapes, has already found that the new phase may have a vanishing excitation energy for single-particle-like excitations.

In the present note we wish to present a qualitative discussion of the general situation, which reveals a remarkable phase diagram [Fig. 3(b)] with an infinity of phases each of which has both metallic and insulating regions. These phases differ from each other by having either different spatial order parameters, different magnetic order, or both.

Our considerations neglect a number of important effects, such as the distortion of the nuclear lattice (regarded as fixed), many-valley effects, imperfections, etc. We are therefore not certain if real physical systems can actually exhibit such a fantastic phase diagram. However, we believe that the general features, at least, of the present discussion are relevant for actual small-gap solids at low temperatures. The entire subject may be viewed as a manifestation of electron-hole instabilities.

We begin by considering a two-band system whose energy-band diagram is schematically shown in Fig. 1(a). The (single) maximum of the valence band is taken at $\vec{k}_a{}^0$, the (single) minimum of the conduction band at $\vec{k}_b{}^0$. We denote the energies of the two bands by $\mathcal{E}_a(\vec{k}-\vec{k}_a{}^0)$, $\mathcal{E}_b(\vec{k}-\vec{k}_b{}^0)$ and write $\vec{w}\equiv\vec{k}_b{}^0-\vec{k}_a{}^0$, $G\equiv\mathcal{E}_b(0)-\mathcal{E}_a(0)$. We assume, as is in fact the case, that the two bands have different anisotropies. For the moment we consider spinless fermions and hence neglect possible magnetic effects.

In a normal insulator there exists a band of collective modes of the electron-hole-pair type, the excitons,[3] with positive excitation energy. That is to say, the maximum binding energy E_B (taken as positive) is less than the gap G.

We now consider what happens when one changes some parameter, α (such as the external pressure), which, in the absence of many-body effects, would reduce the gap G to 0 and then make it negative.

When $G<E_B$ [see Fig. 1(a)], the original ground state becomes unstable against exciton formation and a new type of ground state is formed.[1] The new occupied eigenfunctions are linear combinations of Bloch waves of the original bands,

$$\varphi_{a'}(\vec{k})=u_{\vec{k}}\varphi_a(\vec{k})-v_{\vec{k}}\varphi_b(\vec{k}), \qquad (1)$$

where $\varphi_a(\vec{k})$ and $\varphi_b(\vec{k})$ denote the Bloch func-

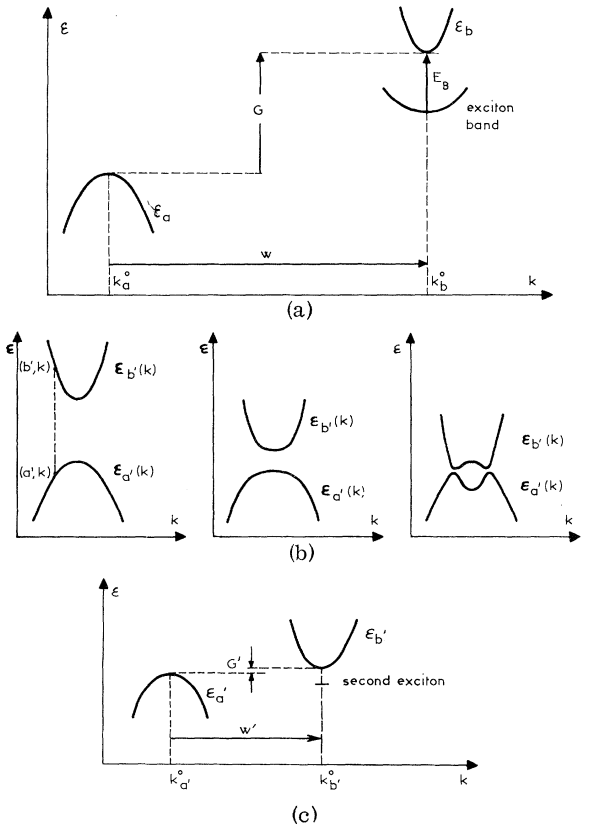

FIG. 1. The insulating side. (a) Energy bands and exciton band of the normal insulator. (b) The new energy bands after the first excitonic transition for successive values of the external parameter (e.g., pressure). (c) The second excitonic instability.

tions of bands a and b with momenta $\vec{k}_a{}^0+\vec{k}$ and $\vec{k}_b{}^0+\vec{k}$. It is evident that in this state there exist components of the charge density which have wave numbers $\pm\vec{w}$, and a corresponding self-consistent potential

$$V'(\vec{r})=\lambda'\cos(\vec{w}\cdot\vec{r}+\gamma), \tag{2}$$

where γ is a phase.[4] In addition to (1) there exist in the new potential, which includes V', excited single-particle states

$$\varphi_{b'}(\vec{k})=v_{\vec{k}}\varphi_a(\vec{k})+u_{\vec{k}}\varphi_b(\vec{k}). \tag{3}$$

We denote the single-particle energies corresponding to (1) and (3) by $\mathcal{E}_{a'}(\vec{k})$ and $\mathcal{E}_{b'}(\vec{k})$ and show these in the left-hand part of Fig. 1(b). We call G' the gap between the new bands.

We now reduce G' further. Eventually the two bands would seem to penetrate each other. However this cannot happen, since the Hamiltonian connects pairs of states $(a',\vec{k})$, $(b',\vec{k})$ with the same k [see, for example, the potential $V'(\vec{r})$, Eq. (2)]. We therefore reach an intermediate stage, shown in the center part of Fig. 1(b), and later a stage shown in the right-hand part of Fig. 1(b). One finds that the gap between $\mathcal{E}_{a'}$ and $\mathcal{E}_{b'}$ becomes the smaller, the deeper the "quasipenetration" of the two bands is. Finally, because of the anisotropy of the bands, the lowest point of $\mathcal{E}_{b'}$, say $\mathcal{E}_{b'}(\vec{k}_{b'}{}^0)$, would become degenerate with the highest point of $\mathcal{E}_{a'}$, say $\mathcal{E}_{a'}(k_{a'}{}^0)$.

In fact, this cannot happen. For just before this we have the situation shown in Fig. 1(c), with an extremely small gap G'. One must now recall the existence of another type of exciton, formed from holes near $\vec{k}_{a'}{}^0$ and from electrons near $k_{b'}{}^0$, with binding energy E_B' against which the previous grounds state becomes eventually unstable, as soon as $G'-E_B'<0$. This leads to a new insulating ground state with occupied wave functions of the form

$$\varphi_{a''}(\vec{k})=u_{\vec{k}}'\varphi_{a'}(\vec{k})-v_{\vec{k}}'\varphi_{b'}(\vec{k}), \tag{4}$$

and energy $\mathcal{E}_{a''}$. The new potential includes, in addition to V', also

$$V''=\lambda''\cos(\vec{w}'\cdot r+\gamma'), \tag{5}$$

where $\vec{w}'=\vec{k}_{b'}{}^0-\vec{k}_{a'}{}^0$, as well as other new terms involving $\vec{w}$ and $\vec{w}'$. In addition there exists also a band of unoccupied states,

$$\varphi_{b''}(\vec{k})=v_{\vec{k}}'(\vec{k})\varphi_{a'}(\vec{k})+u_{\vec{k}}'\varphi_{b'}(\vec{k}), \tag{6}$$

with energy $\mathcal{E}_{b''}$. We note that the situation is completely analogous to that of the first instability.

Hence we conclude, by induction, that starting from the normal insulating state we pass through an infinity of insulating phases before the gap for single-particle excitations finally vanishes. At each state we introduce a new undulation in the charge density and in the potential, such as V' and V'', with new wave vectors $\vec{w}',\vec{w}'',\cdots$ as well as their linear combinations. The wave vectors $\vec{w}',\vec{w}'',\cdots$ become rapidly very small.

Now we make a fresh start from the opposite end. We begin with a normal semimetal shown in Fig. 2(a). $\mathcal{E}_F$ is the Fermi level and the gap $G\equiv\mathcal{E}_b(0)-\mathcal{E}_a(0)$ is now negative. The bands are again assumed to have different anisotropies.

We now change our external parameter α to make $|G|$ smaller and smaller. It can be shown that when the number of carriers becomes

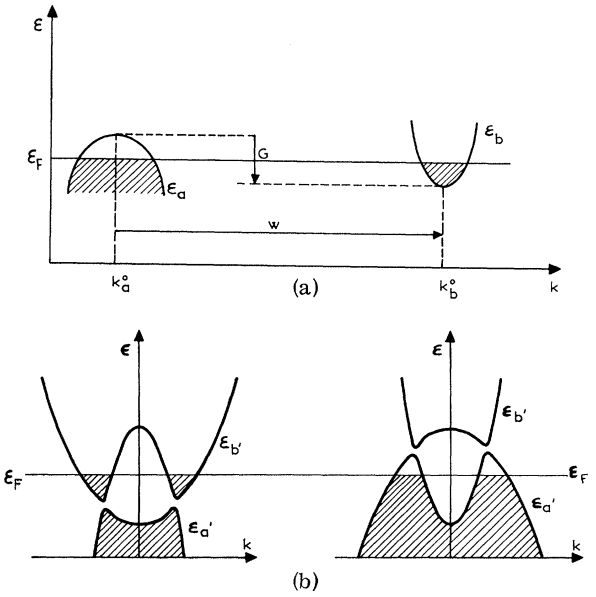

FIG. 2. The metallic side. (a) Energy bands of the normal semimetal. (b) Energy bands after the first Overhauser transition for two different directions of k.

small enough, the normal ground state becomes unstable against the formation of an Overhauser charge density fluctuation[5] of wave vector $\vec{w}$. This may also be regarded as the appearance of bound electron-hole pairs. The resulting self-consistent potential now contains a new term of the form of Eq. (2), and again we have wave functions of the form (1) and (2), and new energy bands $\mathcal{E}_{a'}(\vec{k})$ and $\mathcal{E}_{b'}(\vec{k})$. These are shown in Fig. 2(b), where we show the energy as function of $\vec{k}$ in two different directions (the band anisotropy is essential here). Evidently, we now have a new semimetallic phase.

Changing our parameter α, so as to reduce the number of carriers further, eventually must lead to a new Overhauser instability, which occurs just before the new gap G' becomes zero and involves holes from the vicinity of the new valence-band maximum $\mathcal{E}_{a'}(\vec{k}_{a'}{}^0)$ and electrons from the vicintiy of the new conduction-band minimum, $\mathcal{E}_{b'}(\vec{k}_{b'}{}^0)$. The new potential will, among other terms, contain one of the form of Eq. (5), where $\vec{w}' = \vec{k}_{b'}{}^0 - \vec{k}_{a'}{}^0$ ($|\vec{w}'| \ll |w|$). Again we conclude, by induction, that there will be a succession of an infinite number of metallic phases before the (negative) gap finally vanishes.

Thus, as function of α, we have schematically the situation at $T = 0°$ shown in Fig. 3(a). Here m is the normal semimetallic phase, m', m'', $\cdots$ more and more distorted metallic phases; i is the normal insulating phase and i', i'', $\cdots$ more and more distorted insulating phases.[6] On the basis of the simplest model, previously considered,[1] we tentatively complete the "phase diagram" by adding the temperature dependence of the instabilities. This leads to the schematic phase diagram of Fig. 3(b). The phase boundaries form an infinite nested set. Each phase is characterized by a fixed number of additional wave vectors which occur in the Fourier expansion of the electronic density. In the normal phase, P, this number is 0; in P' it is 1 (the wave vector $\vec{w}$); in P'' it is 2; etc. It will be seen that at $T = 0°$, each phase has a metallic and insulating region. Thus for finite temperature it is not possible meaningfully to describe any phase as either insulating or metallic. We expect the sequence of transition temperatures, $T_C', T_C'', T_C''', \cdots$ to be rapidly decreasing and hence more and more difficult to observe.

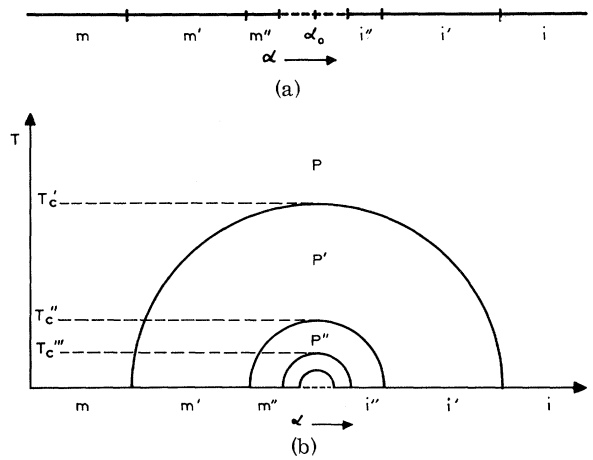

FIG. 3. The excitonic phases. (a) Succession of phases, at $T = 0°$, for different values of α; m, metallic; i, insulating. The dotted interval contains an infinity of m and i phases. (b) Total phase diagram, showing an infinity of nested phases.

A few remarks about the original higher excitonic bands of the normal insulator i. As α is changed towards α_0 [see Fig. 3(a)], the energy bands become altered and hence so do the excitons. Whenever the minimum excitation energy of an exciton band becomes equal to the energy band gap, an excitonic transition of the type discussed will occur.

So far we have neglected spin. When this is included we find the following new possibilities: Starting from the insulating side and with a nonmagnetic phase i, the excitons giving rise to the first instability would be expected to be

often triplet excitons. In that case the new phase i' will have a magnetic order, as will the subsequent phases. Similarly, starting from the metallic side, the first Overhauser instability may well be a spin-density instability,[7] so that the new phase m' will be magnetic, as will subsequent phases. Obviously all kinds of combinations of nonmagnetic and magnetic instabilities are possible.

We suggest that the above considerations provide a framework for the interpretation of distortive and/or magnetic phase transitions of small-gap solids. A fuller account is in preparation.

It is a pleasure to thank the National Science Foundation for the award of a fellowship and Professor J. Friedel and Professor P. Nozières for their hospitality.

[1]N. F. Mott, Phil. Mag. 6, 287 (1961); R. S. Knox, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1963), Suppl. 5, p. 100; L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela. 6, 2791 (1964) [translation: Soviet Phys.—Solid State 6, 2219 (1965)]; J. des Cloiseaux, J. Phys. Chem. Solids 26, 259 (1965); W. Kohn, in Physics of Solids at High Pressure, edtied by C. T. Tamizuka and R. M. Emrick (Academic Press, Inc., New York, 1965), p. 561. D. Jerome, T. M. Rice, and W. Kohn, Phys. Rev. 158, 462 (1967); additional references are given in this paper.

[2]J. Zittartz, Phys. Rev. (to be published); also Office of Naval Research Technical Report No. 45, NONR-2216-(11), Project No. NR 017-630, 1967 (unpublished).

[3]For the moment we consider, for simplicity, only the lowest exciton band of each family. At the end we come back briefly to the excited bands.

[4]Of course a real solid will respond to this potential by a lattice distortion which the present model, with fixed nuclei, does not take into account.

[5]A. W. Overhauser, Phys. Rev. Letters 4, 415 (1960).

[6]It could happen that in passing from, say, m'' to m''', the density fluctuation w' disappears. This would lead to a somewhat different phase diagram than Fig. 3(b).

[7]A. W. Overhauser, Phys. Rev. Letters 4, 462 (1960).

FORMATION OF LOCAL MAGNETIC MOMENTS IN METALS*

H. Suhl
Department of Physics, University of California, San Diego, La Jolla, California
(Received 15 June 1967)

Current theories of local magnetic moment formation in metals are essentially Hartree-Fock theories[1,2] and certain improvements thereon.[3] These theories generally lead to implausibly sharp threshold conditions, and raise certain difficulties due to violation of rotational invariance.

In this note we suggest the possibility of calculating directly the quantities susceptible to measurement, in particular, spin susceptibility, using only standard many-body perturbation theory. The model is a degenerate electron gas described by a Hamiltonian consisting of the kinetic energy, Coulomb interaction, and a structureless impurity potential V.

The spin susceptibility at wave number $\vec{q}$ and frequency Ω, due to a periodic magnetic field of wave number q' and frequency Ω, is the analytic continuation to $\Omega + i\delta$ $(\delta > 0)$ of the function

$$\chi(q,q',\nu_n) = \frac{2(g\mu_B)^2}{\beta^2} \sum_{\omega_1\omega_2} \int \frac{d\vec{p}_1 d\vec{p}_2}{(2\pi)^6} \mathcal{G}^{II}(\vec{p}_1\omega_1, \vec{p}_2\omega_2; \vec{p}_1+\vec{q}, \omega_1+\nu_n; \vec{p}_2-\vec{q}', \omega_2-\nu_n) \qquad (1)$$

from the even points $i\nu_n = 2n\pi i/\beta$, where $\beta = 1/kT$, T is the temperature, and k Boltzmann's constant. $\mathcal{G}^{II}$ is the two-particle Green's function with a "triplet" assignment of spin subscripts (see below). The ω's are the "odd" points $(2n+1)\pi/\beta$. (The notation is that of Abrikosov, Gor'kov, and Dzyaloshinski.[4])

Wolff[2] has treated a "single-band" version of the present Hamiltonian in Hartree-Fock approximation, replacing the total potential $(V + \text{Hartree-Fock})$ by an average over one band. This results in an s-wave scattering problem with a zero-range force. He found a threshold condition on the parameters of the problem, beyond which "up"- and "down"-spin electrons see different Fock fields. We shall eventually perform a similar averaging, but begin with an exact formulation.

The analog of the Wolff condition in many-