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Зарядовое упорядочение в обобщенной модели Хаббарда
в различных приближениях

Выведен обобщенный Гамильтониан электрон-электронного взаимодействия в кристаллической решетке с учетом внутриатомного и межатомного кулоновского и обменного взаимодействия. Учтено электрон-решеточное взаимодействие в приближении, соответствующем узким энергетическим зонам.

На основе плотности состояний найдены в аналитическом виде плотности состояний для ферромагнитного, антиферромагнитного и зарядового упорядочения после включения электронных корреляций.

Для наибольшего внутриатомного, внутризонного кулоновского отталкивания использован метод когерентного потенциала и приближения Хаббарда I и Хаббарда III. Остальные взаимодействия считаются малыми и учтены в рамках метода молекулярного поля.

Расчет критических кривых ферро-, антиферро- и зарядовых упорядочений проводится с помощью метода статической магнитной восприимчивости, в котором используются найденные в аналитическом виде кривые плотности состояний.

Приведенные кривые указывают на то, что в случаях некоторых чисел заполнения электронами зарядовое упорядочение появляется раньше, чем антиферромагнитное или ферромагнитное упорядочение. Этот теоретический вывод поясняет наступление такого упорядочения во многих реальных веществах, как например, Fe_3O_4 , SmS и других.

Сообщение Объединенного института ядерных исследований. Дубна 1979

Mizia J., Richter A.

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On the Charge-Ordered Solution of the
Extended Hubbard Model in Different
Approximations

Critical curves for ferromagnetic, antiferromagnetic and charge-ordered alignments are compared in the Hartree-Fock, first and third Hubbard approximations. These curves are calculated by the method of static magnetic susceptibility for limiting cases of strong and weak (compared to the band-width) Coulomb interaction.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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I. Introduction

The Hubbard model[1] with a repulsive correlation parameter is a well-known model for electrons in a narrow band. A few exact results and many approximate treatments concerning the magnetic and electric properties of this system are known (for a review see Cyrot [2]). The method of coherent potential has been applied to the case of arbitrary band occupation for ferromagnetic (Mizia [3]) and antiferromagnetic solution (Mizia[4]).

The aim of this paper is to discuss the possibility of the charge-ordered state within this method for arbitrary band occupation. Charge-ordered solutions can explain the insulating behaviour of numerous transitions and rare-earth metal chalcogenides (Goodenough[5], Varma[6], Ionova et al.[7]). An attractive electron-electron interaction ($\mathcal{U}<0$) may lead to a charge-ordered phase (Röpke et.al.[8], Mertsching[9], Ionov et al.[10]), whereas in extended models charge-ordered solutions are possible with $\mathcal{U}>0$ in special parameter ranges (Robaszkiewicz[11], Ionova et al.[12]). In the framework of the alloy analogy approximation no charge-ordered solution can be obtained (Brouers [13]). For this reason in this paper the effective mean field is added [3] to the Coulomb electron-electron interaction which is treated in higher approximations.

Inclusion of electron-phonon interaction within the harmonic approximation influences the Coulomb repulsion of electrons [14]. In the case of strong Coulomb interaction $\mathcal{U}$ the band-width is supposed to be unaffected in the lowest approximation. If the electron-phonon coupling is strong enough, an attractive interaction between electrons can occur which yields a charge-ordered state for a periodic lattice distortion. Fluctuations in the effective charge field turn out to be important in this region. They may be relevant in the intermediate valence problem. The influence of an average lattice distortion on the stabilization of a mixed valence state was considered by Sherrington and Riseborough /15/. More involved model systems to discuss this problem are presented in /16/.

2. Hamiltonian and Its Mean Field Approximation

The Hamiltonian for one narrow degenerate band can be written in the form given by Hubbard /17/

$$H=\sum_{ij}\sum_{\mu\nu} t_{ij}^{\mu\nu} c_{i\mu}^{+} c_{j\nu} + \frac{1}{2}\sum_{ijkl}\sum_{\mu\nu pq} (i\mu, j\nu|\tfrac{1}{r}|kp, lq)\, c_{i\mu}^{+} c_{j\nu}^{+} c_{lq} c_{kp} \,. \tag{1}$$

The notation is the same as in /17/. Let us recall only that μ is a label distinguishing the various degenerate subbands and including the spin label.

In the interaction term we shall retain the dominant terms with $i=j=k=l$ or $i=k$, $j=l$ and $i=l, j=k$ corresponding to the intra-atomic, inter-atomic Coulomb and inter-atomic exchange interactions, respectively, what brings up

$$\begin{aligned} H = T &+ \frac{1}{2}\sum_{i}\sum_{\mu\nu pq} (i\mu, i\nu|\tfrac{1}{r}|ip, iq)\, c_{i\mu}^{+} c_{i\nu}^{+} c_{iq} c_{ip} + \\ &+ \frac{1}{2}\sum_{(ij)}\sum_{\mu\nu pq} (i\mu, j\nu|\tfrac{1}{r}|ip, jq)\, c_{i\mu}^{+} c_{j\nu}^{+} c_{jq} c_{ip} + \\ &+ \frac{1}{2}\sum_{(ij)}\sum_{\mu\nu pq} (i\mu, j\nu|\tfrac{1}{r}|jp, iq)\, c_{i\mu}^{+} c_{j\nu}^{+} c_{iq} c_{jp} \,, \end{aligned} \tag{2}$$

where T denotes the kinetic energy, symbol (ij) means the sum over nearest neighbours only. The next biggest terms neglected here are /1/: $(ii|\frac{1}{r}|ij)$, $(ij|\frac{1}{r}|ik)$, $(ii|\frac{1}{r}|jj)$. There is a great variety of different Hamiltonians, which can be derived from the above one. It seems to be reasonable to preserve only terms of the Coulomb type with $p=\mu$, $q=\nu$ and exchange type with $p=\nu, q=\mu$. Taking into account the commutation rules for the operators, replacing the index μ by μ,σ (σ is a spin label) and assuming additionally that the interaction integrals do not depend on spin indices, one obtains

$$\begin{aligned} H = T &+ \frac{1}{2}\sum_{i}\sum_{\substack{\mu\nu\\ \sigma\sigma'}} (i\mu, i\nu|\tfrac{1}{r}|i\mu, i\nu)\, \hat{n}_{i\mu\sigma} \hat{n}_{i\nu\sigma'} - \\ &- \frac{1}{2}\sum_{i}\sum_{\substack{\mu\nu\\ (\mu\neq\nu)\\ \sigma\sigma'}} (i\mu, i\nu|\tfrac{1}{r}|i\nu, i\mu)\, c_{i\mu\sigma}^{+} c_{i\mu\sigma'} c_{i\nu\sigma'}^{+} c_{i\nu\sigma} + \\ &+ \frac{1}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\ \sigma\sigma'}} (i\mu, j\nu|\tfrac{1}{r}|i\mu, j\nu)\, \hat{n}_{i\mu\sigma} \hat{n}_{j\nu\sigma'} - \frac{1}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\ (\mu\neq\nu)\\ \sigma\sigma'}} (i\mu, j\nu|\tfrac{1}{r}|i\nu, j\mu) \times \\ &\times c_{i\mu\sigma}^{+} c_{j\mu\sigma} c_{j\nu\sigma'}^{+} c_{i\nu\sigma'} + \frac{1}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\ (\mu\neq\nu)\\ \sigma\sigma'}} (i\mu, j\nu|\tfrac{1}{r}|j\mu, i\nu)\, c_{i\mu\sigma}^{+} c_{j\nu\sigma'}^{+} c_{i\nu\sigma'} c_{j\mu\sigma} - \\ &- \frac{1}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\ \sigma\sigma'}} (i\mu, j\nu|\tfrac{1}{r}|j\nu, i\mu)\, \hat{n}_{i\mu\sigma} \hat{n}_{j\nu\sigma'} \,. \end{aligned} \tag{3}$$

Let us introduce the following integrals assuming that they are independent of μ, ν indices

$\mathcal{U} = (i\mu, i\mu|\frac{1}{r}|i\mu, i\mu)$, $\mathcal{U}' = (i\mu, i\nu|\frac{1}{r}|i\mu, i\nu)$ for $\mu\neq\nu$,
$I = (i\mu, i\nu|\frac{1}{r}|i\nu, i\mu)$ for $\mu\neq\nu$, $\mathcal{U}'' = (i\mu, j\nu|\frac{1}{r}|i\mu, j\nu)$ and
$I' = (i\mu, j\nu|\frac{1}{r}|j\nu, i\mu)$.

After omitting in eq.(3) from the intra-atomic exchange interaction the spin-flip term with $\sigma'=-\sigma$ (see /18/) and neglecting the small double exchange terms of types $(i\mu, j\nu|\frac{1}{r}|i\nu, j\mu)$ for $\mu\neq\nu$ and

$(i\mu, j\nu|\frac{1}{r}|j\mu, i\nu)$ for $\mu \neq \nu$ one arrives at

$$H=\sum_{ij\sigma} t_{ij}\, c^+_{i\sigma} c_{j\sigma} + \frac{\mathcal{U}}{2}\sum_{i\mu\sigma} \hat{n}_{i\mu\sigma}\, \hat{n}_{i\mu-\sigma} + \frac{\mathcal{U}'}{2}\sum_{i}\sum_{\substack{\mu\nu\\(\mu\neq\nu)\\\sigma\sigma'}} \hat{n}_{i\mu\sigma}\, \hat{n}_{i\nu\sigma'} -$$
$$-\frac{I}{2}\sum_{i}\sum_{\substack{\mu\nu\\(\mu\neq\nu)\\\sigma}} \hat{n}_{i\mu\sigma}\, \hat{n}_{i\nu\sigma} + \frac{\mathcal{U}''}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\\sigma\sigma'}} \hat{n}_{i\mu\sigma}\, \hat{n}_{j\nu\sigma'} - \frac{I'}{2}\sum_{(ij)}\sum_{\substack{\mu\nu\\\sigma\sigma'}} \hat{n}_{i\mu\sigma}\, \hat{n}_{j\nu\sigma'}\,. \qquad (4)$$

Until now we considered the electron-electron interaction in terms of the extended Hubbard model. Additionally, the influence of electron-lattice interactions on the magnetic and charge-ordered state is of particular interest. For this reason, we include the coupling of electrons in a very narrow band to a lattice system in the harmonic approximation

$$H_{ph} + H_{e-ph} = \sum_{\vec{q}} \hbar\omega_{\vec{q}}\, b^+_{\vec{q}} b_{\vec{q}} +$$
$$+\sum_{i\vec{q}} \frac{\hbar\omega_{\vec{q}}}{\sqrt{N}}(\hat{n}_{i\sigma} + \hat{n}_{i-\sigma})\left[\gamma_{\vec{q}}\, e^{i\vec{q}\vec{R}_i} b^+_{\vec{q}} + \gamma^*_{\vec{q}}\, e^{-i\vec{q}\vec{R}_i} b_{\vec{q}}\right], \qquad (5)$$

where $\omega_{\vec{q}}$ is the phonon frequency of the $\vec{q}$-th mode and $\gamma_{\vec{q}}$ is the coupling constant with $\gamma_{\vec{q}} \gtrsim 1$. The lattice state influences not only the one-electron energy, but the Coulomb repulsion energy of electrons, too. After a unitary transformation, which displaces the equilibrium positions of the normal coordinates and leads to the polaron-representation, one obtains for strong electron-phonon coupling the effective Hamiltonian/14/

$$H_{eff} = \sum_{ij\sigma} t_{ij}\, c^+_{i\sigma} c_{j\sigma} + \left(\frac{\mathcal{U}}{2} - E_p\right)\sum_{i\mu\sigma} \hat{n}_{i\mu\sigma}\, \hat{n}_{i\mu-\sigma} -$$
$$- E_p\sum_{i\mu\sigma}(\hat{n}_{i\mu\sigma} + \hat{n}_{i\mu-\sigma}) + \frac{\mathcal{U}'}{2}\sum_{i}\sum_{\substack{\mu\nu\\(\mu\neq\nu)\\\sigma\sigma'}} \hat{n}_{i\mu\sigma}\, \hat{n}_{i\nu\sigma'} - \cdots \qquad (6)$$

where $E_p = \frac{1}{N}\sum_{\vec{k}} \hbar\omega_{\vec{k}}\, |\gamma_{\vec{k}}|^2$ leads to a reduction of the Coulomb repulsion. We restrict ourselves to a renormalization of repulsion energy and a shift in the one-electron energy levels on the atoms. The modification of the electron hopping integrals in a vibrating lattice is discussed in ref./14/.

Now, using the well known mean field approximation: $\hat{n}_A \hat{n}_B \simeq \langle\hat{n}_A\rangle \hat{n}_B + \hat{n}_A \langle\hat{n}_B\rangle$ one finds the following expression

$$H^{h-f}_{eff} = \sum_{ij\sigma} t_{ij}\, c^+_{i\sigma} c_{j\sigma} + \sum_{i\mu\sigma}\big[(\mathcal{U} - 2E_p) n^{-\sigma}_{\mu} - I(p-1)\, n^{\sigma}_{\mu} +$$
$$+ \mathcal{U}'(p-1)(n^{\sigma}_{\mu} + n^{-\sigma}_{\mu}) + pz(\mathcal{U}'' - I')(n^{\sigma}_{\mu,i+l} + n^{-\sigma}_{\mu,i+l})\big]\, \hat{n}_{i\mu\sigma}\,. \qquad (7)$$

Here p means the number of orbitals in the degenerate band, $i+l$ is the nearest neighbour lattice site to site i, z is the number of nearest neighbouring atoms in the lattice and n^{σ}_{μ} is the mean particle number in the $\mu\sigma$ subband. The one-electron energy term of eq. (6) is omitted in (7).

Let us for simplicity assume additionally (Mizia/3/) the existence of the full degeneracy: $\langle\hat{n}_{i\mu\sigma}\rangle \overset{df}{=} n^{\sigma}_{\mu} = \frac{n^{\sigma}}{p} \neq f(\mu)$. Then, index μ can be dropped in eq.(7). As a result, one gets the following Hamiltonian

$$H^{h-f}_{eff} = \sum_{ij\sigma} t_{ij}\, c^+_{i\sigma} c_{j\sigma} + \sum_{i\sigma} M^{\sigma} \hat{n}_{i\sigma}\,, \qquad (8)$$

where the molecular field constant M^{σ} is given by

$$M^{\sigma} = (\mathcal{U} - 2E_p)\, n^{-\sigma}_i - I(p-1)\, n^{\sigma}_i + \mathcal{U}'(p-1)(n^{\sigma}_i + n^{-\sigma}_i) +$$
$$+ pz(\mathcal{U}'' - I')(n^{\sigma}_{i+l} + n^{-\sigma}_{i+l})\,. \qquad (9)$$

For ferromagnetic mode one has $n^{\pm\sigma}_i = n^{\pm\sigma}_{i+l}$, so the constant M^{σ} is independent of i.

Assuming the alternant lattice in which the antiferromagnetic or charge simple alternant orders can occur, one can divide this lattice into two sublattices α and β. Then, the i-th lattice sites can be denoted by α and their nearest neighbours $i+l$ sites by β. So, now from eq.(9) one has

$$M^{\sigma}_{\alpha} = (\mathcal{U} - 2E_p)\, n^{-\sigma}_{\alpha} \mp I(p-1)\, n^{\sigma}_{\alpha} + \mathcal{U}'(p-1)(n^{\sigma}_{\alpha} + n^{-\sigma}_{\alpha}) +$$
$$+ pz(\mathcal{U}'' - I')(n^{\sigma}_{\beta} + n^{-\sigma}_{\beta}) \qquad (10)$$

and

$$M_\beta^\sigma=(\mathcal{U}-2E_p)n_\beta^{-\sigma}-I(p-1)n_\beta^\sigma+\mathcal{U}'(p-1)(n_\beta^\sigma+n_\beta^{-\sigma})+ + pz(\mathcal{U}''-I')(n_\alpha^\sigma+n_\alpha^{-\sigma}). \qquad (11)$$

Among different magnetic modes the following most typical one shall be considered here

$$n_\alpha^{\pm\sigma}=n_\beta^{\pm\sigma}=\frac{n\pm m_F}{2} \qquad (12)$$

$$n_\alpha^{\pm\sigma}=n_\beta^{\mp\sigma}=\frac{n\pm m_{AF}}{2} \qquad (13)$$

$$n_\alpha^{\pm\sigma}=\frac{n+m_Q}{2}\,,\quad n_\beta^{\pm\sigma}=\frac{n-m_Q}{2} \qquad (14)$$

where n is the electron number per atom and indices F, AF, Q are used for ferromagnetic, antiferromagnetic and charge-ordering parameters. Using the above expressions in eqs.(10) and (11) one can easily get the following critical values for ordering in the mean field approximation

$$A_{cr}^{F}=-2\,\frac{dM_\alpha^\sigma}{dm_F}\equiv A_{cr}^{AF}=-2\,\frac{dM_\alpha^\sigma}{dm_{AF}}=\left[I(p-1)+\mathcal{U}-2E_p\right]_{cr}^{F(AF)}\,, \qquad (15)$$

$$A_{cr}^{Q}=-2\,\frac{dM_\alpha^\sigma}{dm_Q}=\left[I(p-1)-\mathcal{U}+2E_p-2(p-1)\mathcal{U}'+2pz(\mathcal{U}''-I')\right]_{cr}^{Q}\,. \qquad (16)$$

Comparison of the two last equations gives the first insight into the role of electron-phonon (E_p) and inter-atomic Coulomb ($\mathcal{U}''$) interactions as favouring the charge-ordered state.

3. Coherent Potential Approximation

3.1. Some basic expressions

The calculations in this approximation use the Slater-Koster state-density function corresponding to the semielliptic band (Velicky et al./19/)

$$F_0(z)=\frac{2}{W}\left[\frac{z}{W}-\sqrt{\left(\frac{z}{W}\right)^2-1}\,\right], \qquad (17)$$

where z is the complex energy and W is the half-band-width.

After including in the system the electron-electron correlations the Slater-Koster function is for ferromagnetic alignment obtained by (Velicky et al./19/)

$$F^\sigma(z)=F_0(z-\Sigma^\sigma), \qquad (18)$$

where Σ^σ is the mass operator (coherent potential).

For (α,β) long-range order including antiferromagnetism as well as the charge-order corresponding transformation has the following form (Plischke and Mattis/20/, Brouers/21/)

$$F_{\alpha(\beta)}^\sigma(z)=\left(\frac{z-\Sigma_{\beta(\alpha)}^\sigma}{z-\Sigma_{\alpha(\beta)}^\sigma}\right)^{1/2}F_0\left(\sqrt{(z-\Sigma_\alpha^\sigma)(z-\Sigma_\beta^\sigma)}\right). \qquad (19)$$

Densities of states corresponding to the above Slater-Koster functions are given by

$$\varrho^\sigma(\varepsilon)=-\frac{1}{\pi}\,\mathrm{Im}\,F^\sigma(z)\Big|_{z=\varepsilon+i0} \qquad (20)$$

for ferromagnetism, and

$$\varrho_{\alpha(\beta)}^\sigma(\varepsilon)=-\frac{1}{\pi}\,\mathrm{Im}\,F_{\alpha(\beta)}^\sigma(z)\Big|_{z=\varepsilon+i0} \qquad (21)$$

for (α,β) alignment.

3.2. State densities in limiting cases.

3.2.1. First Hubbard approximation

This approximation is used here for intra-atomic intra-orbital Coulomb interaction. The other interactions are treated in the molecular field approximation assuming that they are only small perturbation to the Coulomb one.

Then, with the appropriate choice of the origin of energy, $T_i = 0$ (T_i is the atomic energy level) the coherent potential (cf. eq. (36) of /1/) takes on the following form

$$\Sigma^{\sigma}(z) = \frac{z\,\mathcal{U}\,n^{-\sigma}}{z-\mathcal{U}(1-n^{-\sigma})} + M'^{\sigma}, \tag{22}$$

where M'^{σ} is equal to the M^{σ} given by eq.(9) with omitted $\mathcal{U}$ term.

In the strong scattering limit $(\mathcal{U} \gg W)$ one gets from eq.(22) the following simplified expression

$$\Sigma^{\sigma}(z) \simeq -z\,\frac{n^{-\sigma}}{1-n^{-\sigma}} + M'^{\sigma} \tag{23}$$

valid for the lower subband $(\,|\varepsilon| < W + M'^{\sigma})$.

For the (α,β) alternant alignment eq.(23) can be easily generalized

$$\Sigma^{\sigma}_{\gamma}(z) = -z\,\frac{n^{-\sigma}_{\gamma}}{1-n^{-\sigma}_{\gamma}} + M'^{\sigma}_{\gamma}, \tag{24}$$

where $\gamma = \alpha$ or β and $n^{\pm\sigma}_{\gamma}$ are given by eqs.(13) and (14) for antiferromagnetism and charge-order, respectively. Using eqs.(23) or (24) for Σ and semielliptic initial density of states [eq.(17)], one can calculate by transformations (18) or (19) the $F^{\pm\sigma}$ quantities for ferromagnetism or $F^{\pm\sigma}_{\alpha(\beta)}$ for (α,β) alignment. A next step is to obtain the corresponding densities of states by eqs. (20) or (21). The final results are as follows:

$$\rho^{\pm\sigma}_{F}(\varepsilon) = \frac{2}{\pi W}\sqrt{1-\frac{1}{W^2}\left(\frac{\varepsilon}{1-n_{\mp}} - M'^{\pm\sigma}_{F}\right)^2} \tag{25}$$

for ferromagnetism, and

$$\rho^{\pm}(\varepsilon) = \begin{cases} \dfrac{2}{\pi W}\sqrt{\dfrac{\varepsilon_{\mp}}{\varepsilon_{\pm}} - \dfrac{1}{W^2}\,\varepsilon^2_{\mp}} & \text{if } \dfrac{\varepsilon_{\mp}}{\varepsilon_{\pm}} - \dfrac{\varepsilon^2_{\mp}}{W^2} > 0 \\ 0 & \text{otherwise} \end{cases} \tag{26}$$

for (α,β) order. $\rho^{\pm} = \rho^{\pm\sigma}$ for antiferromagnetism and $\rho^{\pm} = \rho_{\alpha(\beta)}$ for charge-ordered state. The energies $\varepsilon_{\pm}$ are

$$\varepsilon_{\pm} = \frac{\varepsilon}{1-n_{\mp}} - M'^{\pm\sigma}_{AF}, \quad \varepsilon_{\pm} = \frac{\varepsilon}{1-n_{\pm}} - M'^{Q}_{\alpha(\beta)} \tag{27}$$

for antiferromagnetism and for the charge-ordered state, respectively.

Above $M'^{\pm\sigma}_{F}$, $M'^{\pm\sigma}_{AF} \overset{df}{=} M'^{\pm\sigma}_{\alpha}$ and $M'^{Q}_{\alpha(\beta)}$ are the $M'^{\pm\sigma}_{\gamma}$ quantities after substitution for $n^{\pm\sigma}_{\alpha(\beta)}$ the values corresponding to a given type of ordering and $n_{\pm} = \frac{n \pm m}{2}$ with omitted subscripts at m .

3.2.2. Third Hubbard approximation (alloy analogy method)

Now the coherent potential $\Sigma^{\sigma}(z)$ is obtained from the equation (Soven /22/, Velicky et al./19/)

$$\sum_{j=1}^{2} P^{\sigma}_{j}\,\frac{\varepsilon^{\sigma}_{j} - \Sigma^{\sigma}(z)}{1-(\varepsilon^{\sigma}_{j} - \Sigma^{\sigma}(z))\,F^{\sigma}(z)} = 0 \tag{28}$$

where the probabilities P^{σ}_{j} and corresponding energies ε^{σ}_{j} are equal to

$$\begin{aligned} P^{\sigma}_{1} &= 1 - n^{-\sigma} & \qquad \varepsilon^{\sigma}_{1} &= M'^{\sigma} \\ P^{\sigma}_{2} &= n^{-\sigma} & \qquad \varepsilon^{\sigma}_{2} &= \mathcal{U} + M'^{\sigma} \end{aligned} \tag{29}$$

Above, again the strongest intra-atomic intra-orbital Coulomb interaction is described in the alloy analogy approximation and the others are treated only as a perturbation in the molecular field approximation (see also Mizia/23/).

In the strong scattering limit $(\mathcal{U} \gg W)$ for energies z lying in the lower subband $(|z| < W + M'^{\sigma})$ one can omit the unity in the second denominator of eq.(28) as the small quantity and arrive at

$$\Sigma^{\sigma}(z) \simeq \xi_1^{\sigma} - \frac{P_2^{\sigma}}{F^{\sigma}} = M'^{\sigma} - \frac{n^{-\sigma}}{F^{\sigma}} \tag{30}$$

After repeating the procedure just described for the first Hubbard approximation with the use of the above self-energy one gets

$$\rho_F^{\pm\sigma}(\varepsilon) = \frac{2}{\pi W}\sqrt{1 - n_{\mp} - (\varepsilon - M_F'^{\pm\sigma})^2/W^2} \tag{31}$$

for ferromagnetism, and

$$\rho^{\pm}(\varepsilon) = \begin{cases} \frac{2}{\pi W}\sqrt{g_{\pm} - \varepsilon_{\mp}^2/W^2} & \text{for } g_{\pm} - \varepsilon_{\mp}^2/W^2 > 0 \\ 0 & \text{otherwise} \end{cases} \tag{32}$$

for (α,β) order, where

$$\varepsilon_{\pm} = \varepsilon - M_{AF}'^{\pm\sigma} \tag{33}$$

and

$$\varepsilon_{\pm} = \varepsilon - M'^{Q}_{\alpha(\beta)} \tag{34}$$

for antiferromagnetism and charge-ordered state, respectively. Factor $g_{\pm}$ is equal to

$$g_{\pm} = \frac{\varepsilon_{\mp}}{\varepsilon_{\pm}}\left(1 - \frac{n}{2}\right) - \frac{m^2}{8\varepsilon_{\pm}^2} + \frac{m}{2\varepsilon_{\pm}^2}\sqrt{\varepsilon_+^2\varepsilon_-^2 - \varepsilon_+\varepsilon_-\left(1 - \frac{n}{2}\right) + \frac{m^2}{16}}\,, \tag{35}$$

where $m = m_{AF}$ or m_Q , respectively.

3.2.3. Hartree-Fock approximation

In the $U \ll W$ limit both the first and third Hubbard approximations applied to the intra-atomic intra-orbital Coulomb interaction reduce to the Hartree-Fock approximation for this interaction. So, now all the molecular fields are summed and one has

$$M_{\gamma}^{\pm\sigma} = U n_{\gamma}^{\mp\sigma} + M_{\gamma}'^{\pm\sigma} \tag{36}$$

and

$$\rho_F^{\pm\sigma} = \frac{2}{\pi W}\sqrt{1 - (\varepsilon - M_F^{\pm\sigma})^2/W^2} \tag{37}$$

$$\rho^{\pm}(\varepsilon) = \begin{cases} \frac{2}{\pi W}\sqrt{\frac{\varepsilon_{\mp}}{\varepsilon_{\pm}} - \varepsilon_{\mp}^2/W^2} & \text{for } \frac{\varepsilon_{\mp}}{\varepsilon_{\pm}} - \varepsilon_{\mp}^2/W^2 > 0, \\ 0 & \text{otherwise} \end{cases} \tag{38}$$

where

$$\varepsilon_{\pm} = \varepsilon - M_{AF}^{\pm\sigma} \tag{39}$$

and

$$\varepsilon_{\pm} = \varepsilon - M^{Q}_{\alpha(\beta)} \tag{40}$$

for antiferromagnetism and charge-ordered state, respectively.

3.3. Susceptibility criteria for different alignments

The possibility for existence of any alignment is investigated now by looking for the divergence of static magnetic susceptibility.

The general formula for the susceptibility has the following form (Fukuyama and Ehrenreich /24/)

$$\chi = \frac{2\mu^2\rho(\varepsilon_F)}{1 + \partial n^{\sigma}/\partial n^{-\sigma}}\,, \tag{41}$$

where μ is the Bohr magneton and $\rho(\varepsilon_F)$ is the paramagnetic-state density on the Fermi level.

As was shown in the preceding section, in the case of initial semielliptic density of states the final densities can be found analytically in some limiting cases. For these cases the derivative in the denominator should be expressed by the state-density function, what gives

$$\chi = \frac{2\mu^2\rho(\varepsilon_F)}{1-2\frac{\partial}{\partial m}\int_{-\infty}^{\varepsilon_F}\rho(\varepsilon)\,d\varepsilon} \, . \tag{42}$$

The derivative in the denominator is taken in the paramagnetic limit. Different densities of states calculated above for different types of alignment and for different approximations can be used in this simple formula.

For $U \ll W$ the Hartree-Fock approximation is used for all interactions. Equating to zero the denominator in eq. (42) and using density of states given by eq. (37), one gets the generalized Stoner -Wohlfarth criterion for ferromagnetism:

$$A_{cr}^{F}\,\rho(\varepsilon_F) \geq 1, \tag{43}$$

where

$$\rho(\varepsilon_F) = \frac{2}{\pi W}\cos\varphi_F \tag{44}$$

and A_{cr}^{F} is given by eq.(15).

The Fermi energy is estimated from the condition that

$$n = 2\int_{-\infty}^{\varepsilon_F}\rho(\varepsilon)\,d\varepsilon = \frac{4}{\pi W}\int_{-W+M_p}^{\varepsilon_F}\sqrt{1-(\varepsilon-M_p)^2/W^2}\,d\varepsilon, \tag{45}$$

where $\rho(\varepsilon)$, M_p are the paramagnetic limits of $\rho_F^{\pm\sigma}(\varepsilon)$, $M_F^{\pm\sigma}$. After substituting $\sin\varphi=(\varepsilon-M_p)/W$ and integrating the last expression takes the following form

$$\pi(n-1) = 2\varphi_F + 2\sin\varphi_F\cos\varphi_F \stackrel{df}{=} L(\varphi_F) \tag{46}$$

φ_F estimated from this condition should be inserted into the eq.(42) for the state-density function.

For (α,β) alignments the densities given by eq.(38) together with eqs.(39) and (40) should be used in the denominator of eq.(42).

After equating the latter to zero one arrives at the following conditions

$$A_{cr}^{AF} \geq \frac{1}{K^{0}(n)}, \quad A_{cr}^{Q} \geq \frac{1}{K^{0}(n)}, \tag{47}$$

where A_{cr}^{AF} and A_{cr}^{Q} are given by eqs.(15), (16) and

$$K^{0}(n) = \frac{2}{\pi W}\ln\left|\frac{1+\cos\varphi_F}{\sin\varphi_F}\right| - \rho(\varepsilon_F) \tag{48}$$

The numerical results for the critical constants in this approximation are drawn in fig. 1.

For the first Hubbard approximation in the limit the densities of states given by eqs. (25) to (27) should be used. After the same manipulation as described above one arrives at the following conditions for alignments

$$A'^{F}_{cr}\,\rho(\varepsilon_F) \geq 1 - 2\,\frac{\varphi_F + \pi/2}{\pi} + \frac{n}{2-n} \tag{49}$$

$$A'^{AF}_{cr} \geq \frac{1-n}{1-n/2}\cdot\frac{1}{K_{I}^{\infty}(n)} \tag{50}$$

$$A'^{Q}_{cr} \geq \frac{1}{(1-\frac{n}{2})(1-n)}\cdot\frac{1}{K_{I}^{\infty}(n)} \tag{51}$$

with

$$K_{I}^{\infty}(n) = \frac{2}{\pi W}\ln\left|\frac{1+\cos\varphi_F}{\sin\varphi_F}\right| - \rho(\varepsilon_F), \tag{52}$$

where

$$\rho(\varepsilon_F) = \frac{2}{\pi W}\cos\varphi_F \, . \tag{53}$$

In all A'_{cr} the U constant is omitted as for this interaction the strong scattering approximation is used.

The Fermi energy is estimated now from the slightly changed condition

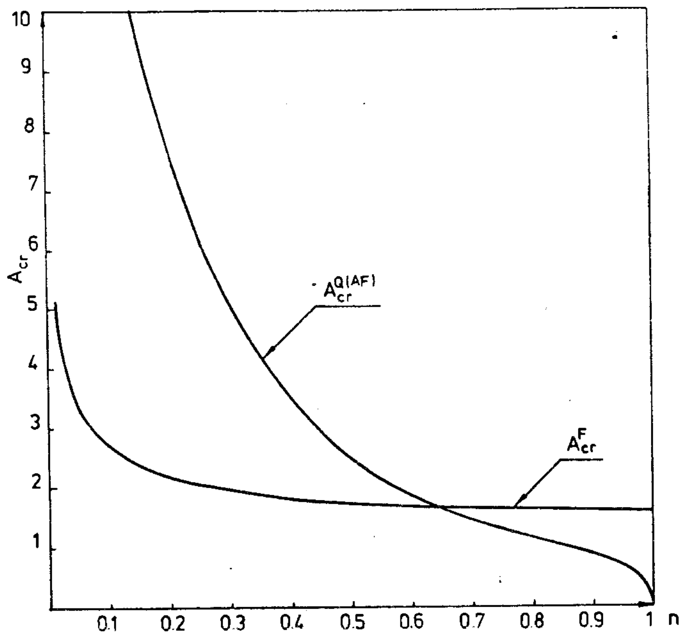

Fig. 1. The critical constants of molecular fields, A_{cr}, given by eqs. (15) and (16) required for ferromagnetic (F), antiferromagnetic (AF), and charge (Q) orderings. The Hartree-Fock approximation is used for all interactions.

$$n = 2\int_{-\infty}^{\varepsilon_F} \rho(\varepsilon)\, d\varepsilon = \frac{4}{\pi W}\int_{(-W+M_p')/(1-\frac{n}{2})}^{\varepsilon_F} \sqrt{1-\left(\frac{\varepsilon}{1-\frac{n}{2}} - M_p'\right)^2/W^2}\, d\varepsilon \,, \qquad (54)$$

where M_p' is the paramagnetic limit of $M_F'^{\pm\sigma}$ given by eq.(9) with $\mathcal{U}$ term omitted. Integrating the last equation gives the following condition for φ_F (where $\sin\varphi_F = \left(\frac{\varepsilon}{1-\frac{n}{2}} - M_p'\right)/W$)

$$\pi\,\frac{3n-2}{2-n} = L(\varphi_F)\,. \qquad (55)$$

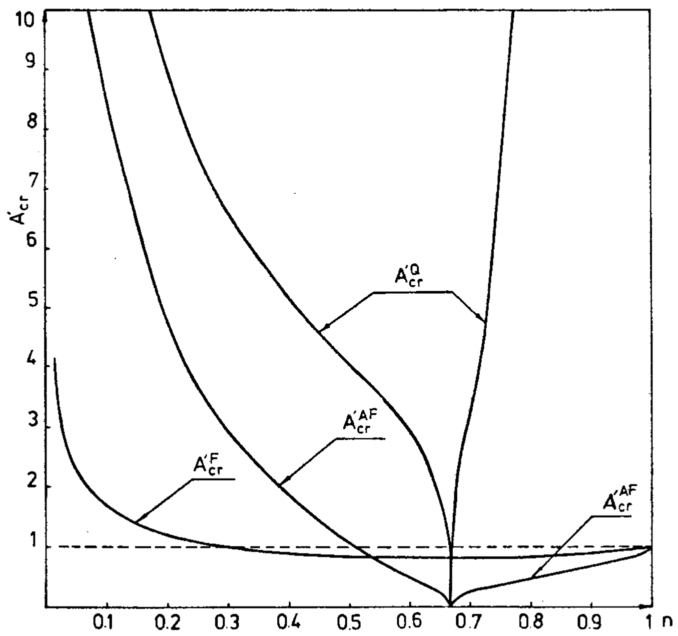

Fig. 2. The critical constants of molecular fields, A'_{cr}, given by eqs. (15) and (16) with omitted $\mathcal{U}$, required for different types of alignments. Indices F, AF, Q are used for ferromagnetism, antiferromagnetism, and charge-order, respectively. For the strong intra-atomic intra-orbital Coulomb interaction $(\mathcal{U} \gg W)$ the first Hubbard approximation is used.

Calculating for given n the φ_F value from this equation and inserting it into eqs. (49) to (53), one arrives at critical constants for different alignments. These values are drawn in fig. 2.

For the third Hubbard approximation in the $\mathcal{U} \gg W$ limit the criteria of alignments calculated on the basis of the state densities given by eqs. (31) to (35) take on the following forms

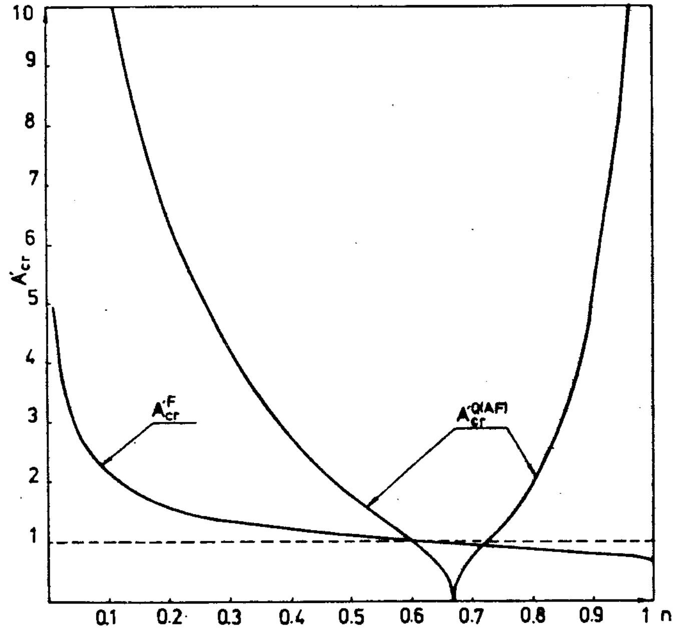

Fig. 3. The critical constants of molecular fields, A'_{cr} , given by eqs. (15) and (16) with omitted $\mathcal{U}$, required for different types of alignments. Indices F, AF, Q are used for ferromagnetism, antiferromagnetism and charge-order, respectively. For the strong intra-atomic intra-orbital Coulomb interaction $(\mathcal{U} \gg W)$ the third Hubbard approximation is used.

$$A'^{F}_{cr}\, \varrho(\varepsilon_F) \geq 1 - \frac{\varphi_F + \pi/2}{\pi} \tag{56}$$

$$A'^{AF}_{cr} \geq \frac{1}{K^{\infty}_{\underline{III}}(n)} \tag{57}$$

$$A'^{Q}_{cr} \geq \frac{1}{K^{\infty}_{\underline{III}}(n)} \tag{58}$$

with

$$K^{\infty}_{\underline{III}}(n) = \frac{2}{\pi W}\sqrt{1-\frac{n}{2}}\, \ln\left|\frac{1+\cos\varphi_F}{\sin\varphi_F}\right| - \varrho(\varepsilon_F), \tag{59}$$

where

$$\varrho(\varepsilon_F) = \frac{2}{\pi W}\sqrt{1-\frac{n}{2}}\cos\varphi_F\ .$$

The Fermi energy and its parameter φ_F (where $\sin\varphi_F = \frac{\varepsilon_F - M'_F}{W\sqrt{1-\frac{n}{2}}}$) can be calculated by integrating the slightly changed distribution

$$\lim_{m\to 0} \varrho^{s}(\varepsilon) = \varrho(\varepsilon) = \frac{2}{\pi W}\sqrt{1-\frac{n}{2} - (\varepsilon - M'_p)^2/W^2}, \tag{60}$$

and the result is the same as previously, so the condition given by eq.(55) holds.

The numerical results obtained in this approximation are drawn in fig. 3.

4. Discussion

As is seen from figs. 2 and 3, any Hubbard approximation does not lead to any alignment without adding molecular field. But the comparison with fig. 1 shows that the interaction treated in the first or third Hubbard approximation (here the Coulomb one) decreases the strength of molecular field required to produce any alignment.

The strength of this minimal molecular field required for alignment is different for different electron numbers per atom and for different approximations. There are some points ($n=\frac{2}{3}$ and $\frac{4}{3}$ for $\mathcal{U} \gg W$ and $n = 0{,}5$ for $\mathcal{U} \ll W$) in the vicinity of which the (α,β) alignment is favoured against the ferromagnetic order both in the first and third Hubbard approximations. Moreover, if ferromagnetic and (α,β) modes are simultaneously possible, then the energy of (α,β) alignment is always lower than that of ferromagnetic one.

The type of the (α,β) alignment preferred (charge-order or antiferromagnetism) depends on the approximation used and also on the relative strength of different interactions which were summed up to give the whole molecular field. Comparing eqs. (15) and (16) one can say that the intra-atomic intra-orbital Coulomb interaction points to the antiferromagnetic alignment, if it is not too strong, and for this reason can be treated in the Hartree-Fock approximation. But, if it becomes strong $(\mathcal{U} \gg W)$, it should be correctly treated in the alloy analogy approximation (third Hubbard approximation) in which there is no difference between critical molecular fields required for charge-order and for antiferromagnetism. Nevertheless, both the modes are not on the same footing, because their molecular fields [eqs. (15) and (16) with omitted $\mathcal{U}$] are composed of different interaction constants. Namely, the electron-phonon and inter-atomic Coulomb interactions prefer the charge-order state whereas the intra-atomic inter-orbital Coulomb and inter-atomic exchange interactions, the antiferromagnetism.

In the first Hubbard approximation in the $\mathcal{U} \gg W$ limit molecular field for antiferromagnetism is much lower than for the charge-ordered state. This is the main difference in the results of the first and third Hubbard approximations.

Charge-ordered states are observed in compounds containing ions with different valence /5/,/6/,/7/. For example, the two species of Fe-ions 2^+ and 3^+ in Fe_3O_4 exist physically separated and form some kind of superlattice as in the charge-ordered system. Besides, homogeneously-mixed valence compounds have been considered recently /6/. In these systems the electron coupling to longitudinal optical phonons dominates. Here it may be possible

that the system undergoes a phase transition to a charge-ordered state. However, experiments show that, for example, SmS is not an insulater in this phase. Valence fluctuations turn out to be important. It should be noted that fluctuations in the effective-charge field are important and relevant to the intermediate-valence problem. Similar aspects were presented for the Anderson model with a localized electron-phonon interaction /25/.

References

1. Hubbard J. Proc.R.Soc. A276, 1963, 238.
2. Cyrot M. Physica 91B, 1977, 141.
3. Mizia J. phys.stat.sol. (b) 74, 1976, 461.
4. Mizia J. phys.stat.sol. (b) 84, 1977, 449.
5. Goodenough J.B. Phys.Rev. 117, 1960, 1442.
6. Varma C.M. Rev.Mod.Phys. 48, 1976, 219 for a recent review see also: Proc. Int.Conf. on Valence Instabilities and Related Narrow-Band Phenomena, Ed. R.D.Parks, Plenum Press, N.Y. 1977.
7. Ionova G.V., Makarov E.F., Pachev O.M., and Ionov S.P. phys.stat.sol., (b) 85, 1978, 683.
8. Röpke G., Albani B. and Schiller W. phys.stat.sol. (b) 69, 1975, 45.
9. Mertsching J. phys.stat.sol. (b) 82, 1977, 289.
10. Ionov S.P., Lubimov V.S., Ionova G.V., Uimin G.V. and Makarov E.F. phys.stat.sol. (b) 72, 1975, 515.
11. Robaszkiewicz S. phys.stat.sol. (b) 76, 1976, K127.
12. Ionova G.V., Makarov E.F. and Ionov S.P. phys.stat.sol. (b) 81, 1977, 671.

13. Brouers F. J.Phys.F, Metal Phys. 7, 1977, L87.
14. Kapustin V.A. VII-th Autumn School on Magnetism, Gauig, 1976.
15. Sherrington D. and Riseborough P. J.Physique 37, 1976, C4-255.
16. Khomskii D.I., Solid State Comm. 27, 1978, 775.
    Ghatak S.K. and Bennemann K.H. J.Phys.F, Metal Phys. 8, 1978, 571.
    Avignon M., Brouers F. and Bennemann K.H. Preprint, Berlin 1978.
17. Hubbard J. Proc. R.Soc. A277, 1964, 237.
18. Raimes S. Many-Electron Theory, North-Holland Publ. Co., Amsterdam/London 1972.
    Hodges L., Ehrenreich H. and Lang N.D. Phys.Rev. 152, 1966, 505.
19. Velicky B., Kirkpatrick S. and Ehrenreich H. Phys.Rev. 175, 1968, 747.
20. Plischke M. and Mattis D. Phys.Rev. B7, 1973, 2430.
21. Brouers F. phys.stat.sol. (b) 76, 1976, 145.
22. Soven P. Phys.Rev. 156, 1967, 809.
23. Mizia J. Physica (Utrecht) 90B, 1977, 179.
24. Fukuyama H. and Ehrenreich H. Phys.Rev. B7, 1973, 3266.
25. Riseborough P.S. Proc. Int. Conf. on Valence Instabilities and Related Narrow-Band Phenomena, Ed. Parks R.D., Plenum Press, N.Y. 1977.

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