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METAL-INSULATOR TRANSITION IN A TWO-BAND HUBBARD-MODEL WITH APPLICATION TO VO

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Переход металл-изолятор в двухзонной модели Хаббарда с применением к окислу *VO*

Рассматривается модель электронной системы, состоящей из двух узких электронных зон при учете их гибридизации. Показано, что в такой модели существует переход металл-изолятор, связанный со скачком проводимости. Обсуждается аналогия с неустойчивостью Лифшица. В качестве возможного примера такого перехода рассмотрены свойства *VO* - проведены качественные и количественные оценки.

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Metal-Insulator Transition in a Two-Band Hubbard-Model with Application to *VO*

A model is considered containing two hybridizied narrow electron bands. It is shown, that in such a model a metal-insulator transition occurs, connected with a jump of the conductivity. Some analogies to the Lifshitz instabilities are discussed. As a possible example for such a behaviour the properties of *VO* are studied qualitatively and quantitatively.

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1. Introduction

To describe the electron correlation in narrow bands the Hubbard-model

$$H_{\text{Hubbard}} = \sum_{ij\sigma} T_{ij}\, c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}\,, \quad n_{i\sigma} = c_{i\sigma}^{+} c_{i\sigma} \qquad (1)$$

(Hubbard 1963) is frequently used. This model describes an isolated s-band; $c_{i\sigma}^{+}$, $c_{i\sigma}$ are the creation and annihilation operators for an electron of spin σ in the Wannier state at the i-th lattioe site, respectively, T_{ij} is the hopping integral, and U describes the electron-electron interaction between two electrons of opposite spins oocupying the same lattice site. The operator (1) is used, for instance, to discuss the metal-insulator transition, occuring by some oxides, sulfides and selenides of transition metals, on the basis of the electron correlation (Cyrot 1970, Weller 1972). Usually instead of the conductivity the occurance of gaps in the one-particle density of states

$$D(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \frac{1}{N} \sum_{\underline{k}\sigma} G_{\underline{k}\sigma}(\varepsilon + i\delta), \quad \delta \geq 0 \qquad (2)$$

with

$$G_{\underline{k}\sigma}(\varepsilon) = \ll c_{\underline{k}\sigma}\,;\, c_{\underline{k}\sigma}^{+} \gg_{\varepsilon} \qquad (3)$$

(we use the notations given by Zubarev (1960)) is considered. For the Fermi energy ε_F inside the gap the system is denoted to be an insulator, for ε_F inside the band — to be a metal. Unfortunately there are considerable difficulties to obtain reasonable solutions for $G_{k\sigma}(\varepsilon)$ in the interesting region $U/w \approx 1$ ($2w$ = bandwidth of T_{ij}); hence the results obtained by different authors do not agree with respect to existence and type of such phase transitions. Usually one gets a phase transition of second order (see, e.g. Cyrot 1970). This is in contradiction to the experiments showing generally a jump in the conductivity and some hysteresis effects. An interesting way to obtain theoretically such a jump is recently proposed by Weller (1972), considering instabilities of the electronic system in analogy to the so-called Lifshitz-instabilities (Lifshitz 1960).

In the present paper instead of (1) a two-band model is considered in the form

$$H = \sum_{\nu=1}^{2} H^{\nu} + H^{12},$$

$$H^{\nu} = \sum_{ij\sigma} T_{ij}^{\nu} c_{i\sigma\nu}^{+} c_{j\sigma\nu} + U^{\nu} \sum_{i} n_{i\uparrow\nu} n_{i\downarrow\nu}, \qquad (4)$$

$$H^{12} = \sum_{ij\sigma} \left[\Delta_{ij} c_{i\sigma 1}^{+} c_{j\sigma 2} + \text{h.c.} \right].$$

The aim is to demonstrate, that in such a model a metal-insulator transition can occur, in connection with a jump in the conductivity, with a change in volume, and therefore with some hysteresis effects. In contradiction to the above mentioned situation in the s-band model (1), the results of the model (4) are rather independent of the approximations used.

The operator (4) describes systems with two narrow bands, which may be strong coupled. Examples are VO, TiO, CrO, and some sulfides and selenides. The foundation of the operator (4) in the case of VO is discussed in the next section of this paper.

Two-band models of the type (4) or in similar form are discussed by several authors (Harris and Lange 1967, Sokoloff 1970), but they considered only bands isolated from each other. The case of completely degenerated bands is discussed by Schneider, Heiner and Haubenreisser (1972), using a pure Hubbard like interaction between the bands. In contradiction to those papers, in the present paper the case of different bands with strong overlapping and strong hybridization is considered.

2. Foundation of the model operator

2.1. Experimental situation in VO

For the system VO_x with $0.80 < x < 1.30$ a lot of experimental results is known. Extended reviews on

this matter are given by Adler (1968) and Goodenough (1972). Unfortunately there are considerable difficulties connected with the preparation of samples, so that for the case $x = 1.00$ considered here the results obtained by different authors do not agree. In some experiments (Morin 1959, Warren et.al. 1967) a metal-insulator transition was observed with a transition temperature $T_M = 126\,°K$, connected with a jump of the conductivity of the order 10^6. Other authors have not found such a transition (Kawano et.al. 1966, Warren et.al.1970). Altogether the experimental results for the conductivity in this region differ by several orders of magnitude, presumably the different samples did not contain pure VO, but rather a mixture of several oxides, mainly V_2O_3, and pure V, essentially influencing the properties (Adler 1968). Therefore it may be of considerable interest to discuss the properties of VO obtained on the basis of theoretical models.

The experiments agree in the following points: VO has a rocksalt structure (crystal parameter $a = 4.1\,\text{Å}$), the Fermi energy lies in the centre of the t_{2g}-subband, and this t_{2g}-band is well isolated from all other bands (e_g, s- and p- band). This situation agrees also with theoretical calculations (Tewari 1972, Heine and Mattheiss 1971). Furthermore there are nearly 16% randomly distributed vacancies (Adler 1968, Goodenough

1972, Mott 1971), as well at the V- sites as at the C-sites. By these vacancies a trap-band is caused, observed in many experiments (see,e.g. Goodenough 1972).From these properties a simple model can be derived, applicable also to similar systems (TiO, CrC).

2.2 Two-band description+

We consider the usual Hamiltonian describing the electronic system:

$$H = \sum_{ij\sigma} T_{ij}\, c_{i\sigma}^{+} c_{j\sigma} + \sum_{ijlm,\sigma\sigma'} V_{ijlm}\, c_{i\sigma}^{+} c_{j\sigma'}^{+} c_{l\sigma'} c_{m\sigma} \qquad (5)$$

Since narrow bands are discussed, the interaction matrix V_{ijlm} of (5) has the properties, generally studied by Hubbard (1963). Following him, only the interaction between electrons occupying the same lattice site is taken into account, that means

$$V_{ijlm} \longrightarrow \tfrac{1}{2} U \delta_{ij} \delta_{jl} \delta_{lm} . \qquad (6)$$

+To avoid misunderstanding: the author does not claim to solve the problem of vacancies in this unusual way. The considerations of this subsection are only used to motivate the two-band model.

The overscript ν ($= 1$ or 2) denotes the fact, that the lattice sites i are related to a certain subsystem (occupied or vacant sites, respectively).

The kinetic energy part of (5) can be approximated by an Anderson operator (Anderson 1958), where the difference between the diagonal elements of T_{ij} describes the different potentials at occupied and vacant sites:

$$T_{ii} = \varepsilon^{\nu} \equiv \begin{cases} \varepsilon^{occ} \\ \varepsilon^{vac} \end{cases} \quad \text{if } i \text{ is related to } \nu = \begin{matrix} 1 \\ 2 \end{matrix} . \tag{7}$$

For convenience the zero point of the energy can be ohosen in such manner, that

$$\varepsilon^{occ} = 0, \qquad \varepsilon^{vac} \equiv \omega_0 . \tag{8}$$

Considering the case $U^{\nu} = 0$, the subsystems can be described by a density of states, which can be obtained using the coherent potential approximation (CPA) (Soven 1967, Velicky et.al.1968). If the density of states $D_0(\varepsilon)$ of the "ideal" crystal (without vacancies, $c = 0$) is written in the form

$$D_0(\varepsilon) = 3 f(\varepsilon, w), \tag{9}$$

$$\int d\varepsilon f(\varepsilon, w) = 1, \quad f(\varepsilon, w) = 0 \text{ if } |\varepsilon| > w,$$

then the local CPA-densities are defined by

$$D_0^{\nu}(\varepsilon) = -\frac{A^{\nu}}{\pi} \operatorname{Im} \frac{G^{CPA}(\varepsilon)}{1 - (\varepsilon^{\nu} - W) G^{CPA}(\varepsilon)} , \tag{10}$$

where the coherent potential W is given by

$$W = c\,\omega_0 + W(\omega_0 - W)\, G^{CPA}(\varepsilon),$$

$$G^{CPA}(\varepsilon) = \int d\varepsilon' \frac{f(\varepsilon', w)}{\varepsilon - W - \varepsilon'} . \tag{11}$$

A^{ν} in (10) is the oocupation number of the ν-th subband,

$$A^{\nu} = \begin{cases} 3 - c \\ c \end{cases} \quad \text{if } \nu = \begin{matrix} 1 \\ 2 \end{matrix} \tag{12}$$

c is the conoentration of vacanoies ($c \approx 0.16$ in VO), and w describes the band width of the "ideal" crystal.

In this form one obtains a two-band description of the discussed system, in agreement with experimental densities of states (Goodenough 1972). Generally both the subbands overlap, since the shift between the centres of the bands is smaller than the band width w. Furthermore the subbands are strong hybridizied; the matrix elements Δ_{ij} arise from the transition elements T_{ij} between the sites of different subsystems.

Using this desoription, VC is an example for a two-band model, described by the operator (4).

2.3. Model parameters

In this subsection the most essential properties of the densities of states $D_o^\nu(\varepsilon)$ of both the subsystems ν are discussed. Furthermore the influence of pressure is considered.

To obtain approximate expressions for the densities of states $D_o^\nu(\varepsilon)$ from (1o), we use the moments

$$M_n^\nu = \int d\varepsilon\, \varepsilon^n D_o^\nu(\varepsilon) \qquad (13)$$

up to $n = 2$. M_o^ν is given by the A^ν from (12), the first moment is related to the centres of the bands which are given by the corresponding atomic levels. Since M_2^ν is defined by the band width w^ν of the ν - th subband, it is possible to write

$$D_o^\nu(\varepsilon) \approx A^\nu f(\varepsilon - \omega_\nu \delta_{\nu,2}, w^\nu) \qquad (14)$$

with $f(\varepsilon, w)$ from (9).(By the way, using a parabolic density of states, this is the exaot solution of (1o) in the case $\omega_o \longrightarrow \infty$.)

In (14) the band widths w^ν are needed. Since in first order the band widths are related to the number of nearest neighbours z in the form

$$w^\nu \sim z^\nu \sim \begin{cases} 1-c & \text{if } \nu = 1 \\ c & \text{if } \nu = 2 \end{cases} \qquad (15)$$

one obtains

$$w^\nu = \begin{cases} (1-c)w & \text{if } \nu = 1 \\ cw & \text{if } \nu = 2 \end{cases} \qquad (16)$$

in agreement with measurements (Goodenough 1972).

Of course, using the CPA-densities of states (1o) or (14), band tails up to the full width w of the original band are neglected. However, the density of states of these tails is very small, hence, following Mott (1971), the corresponding states are well localized and are not important in the further considerations.

Changing the crystal parameter a, perhaps in dependence on presssure p, the most parameters of

the model change. This changing can be expressed by the compressibility

$$\varkappa_0 = -\frac{1}{v}\frac{\partial v}{\partial p}\Big|_T = -\frac{3}{a}\frac{\partial a}{\partial p}\Big|_T . \qquad (17)$$

Considering the dimension of the different parameters it follows

$$\frac{\partial w^\nu}{\partial p} = \gamma_w \varkappa_0 w^\nu , \quad \frac{\partial U^\nu}{\partial p} = \gamma_U \varkappa_0 U^\nu , \gamma_w \approx \frac{2}{3} > \gamma_U \approx \frac{1}{3} > 0. \qquad (18)$$

Δ_{ij} shows the same dependence on p as the band widths.

3. One-particle properties

3.1. Green's functions

The Green's functions

$$G_{ij\sigma}^{\nu\nu'}(\omega) = \ll c_{i\sigma\nu} ; c_{j\sigma\nu'}^{+} \gg_\omega \qquad (19)$$

and

$$\Gamma_{ij\sigma}^{\nu\nu'}(\omega) = \ll n_{i-\sigma\nu} c_{i\sigma\nu} ; c_{j\sigma\nu'}^{+} \gg_\omega / \langle n_{i-\sigma\nu} \rangle \qquad (20)$$

are needed in the following. With H from (4) the equations of motion

$$[H, c_{i\sigma\nu}] = -\sum_j T_{ij}^{\nu} c_{j\sigma\nu} - U^\nu n_{i-\sigma\nu} c_{i\sigma\nu} - \sum_j \Delta_{ij} c_{j\sigma\bar{\nu}} , \qquad (21)$$

$$[H, n_{i-\sigma\nu} c_{i\sigma\nu}] \approx -\langle n_{i-\sigma\nu} \rangle \sum_{j(\neq i)} T_{ij}^{\nu} c_{j\sigma\nu} -$$

$$-(U^\nu + T_{ii}^{\nu}) n_{i-\sigma\nu} c_{i\sigma\nu} - \langle n_{i-\sigma\nu} \rangle \sum_j \Delta_{ij} c_{j\sigma\bar{\nu}} \qquad (22)$$

follow (with $\bar{\nu} \neq \nu$). In (22) the kinetic energy part is decoupled using Hubbard's procedure (Hubbard 1963). This approximation is usable, since here is not discussed the manner of the appearance of gaps (these essentially remain unchanged in the further calculations).

Only the fact is used, that gaps exist, which is right, however, at sufficiently large U, independent of the used approximations (Harris and Lange 1967).

In (22) the hybridization term is decoupled analogously to the hopping energy, since both terms are of the same order of magnitude. From (21) and (22) a closed system of equations for $G(\omega)$ and $\Gamma(\omega)$ follows, which can be solved straightforwardly. For the paramagnetic case ($\langle n_{i\sigma\nu} \rangle = n^\nu/2$, $n^\nu = \langle n_{i\uparrow\nu} + n_{i\downarrow\nu} \rangle$) +)

$$G^{\nu\nu}_{\underline{k}\sigma}(\omega) = \left[F^\nu(\omega) - \varepsilon^\nu_{\underline{k}} - \frac{|\Delta_{\underline{k}}|^2}{F^{\bar\nu}(\omega) - \varepsilon^{\bar\nu}_{\underline{k}}} \right]^{-1} \quad (23)$$

is obtained, with the expression

$$F^\nu(\omega) = \left[\frac{1 - n^\nu/2}{\omega - \omega_0 \alpha_{\nu,2}} + \frac{n^\nu/2}{\omega - \omega_0 \alpha_{\nu,2} - U^\nu} \right]^{-1}, \quad (24)$$

known from Hubbard's decoupling procedure. The $\varepsilon^\nu_{\underline{k}}$ are the Fourier transformation of $T^\nu_{ij}(1-\alpha_{ij})$ with

+) The application of these considerations to the ferromagnetic or antiferromagnetic state is possible in the same way, but with additional effort.

T^ν_{ij} from (4). In the case of $V0$ the subbands were obtained using the CPA. Therefore, the $\varepsilon^\nu_{\underline{k}}$ are the (complex) one-particle energies corresponding to the CPA-density of states $D^\nu_0(\varepsilon)$ of (14). $\Delta_{\underline{k}}$ is the Fourier transformation of Δ_{ij}.

The other Green's functions follow from (23) by

$$G^{\bar\nu\nu}_{\underline{k}\sigma}(\omega) = \frac{\Delta^*_{\underline{k}}}{F^{\bar\nu}(\omega) - \varepsilon^{\bar\nu}_{\underline{k}}} G^{\nu\nu}_{\underline{k}\sigma}(\omega), \quad \Gamma^{\nu\nu}_{\underline{k}\sigma}(\omega) = \frac{\omega - \omega_0 \alpha_{\nu,2}}{\omega - \omega_0 \alpha_{\nu,2} - U^\nu(1-n^\nu/2)} G^{\nu\nu}_{\underline{k}\sigma}(\omega) \quad (25)$$

3.2. Density of states

Analogously to (2) from (23) the densities of states $D^\nu(\varepsilon)$ follow. Closed expressions can be obtained, if the similarity between the subbands (14) is used, and if the matrix elements $\Delta_{\underline{k}}$ are assumed to be independent of $\underline{k}$, i.e. $\Delta_{\underline{k}} \to \Delta$. Since in (23) the hybridization is important only in a small region of $\underline{k}$, this approximation, essentially simplifying the further calculations, is usable. If follows

$$D^\nu(\varepsilon) = A^\nu \frac{\left(\frac{F^\nu(\varepsilon)}{\alpha^\nu} - B(\varepsilon)\right) f(\omega^\nu A(\varepsilon), w^\nu) - \left(\frac{F^\nu(\varepsilon)}{\alpha^\nu} - A(\varepsilon)\right) f(\omega^\nu B(\varepsilon), w^\nu)}{A(\varepsilon) - B(\varepsilon)} \quad (26)$$

where $\alpha^\nu = w^\nu / w$, and

$$\left.\begin{matrix} A(\varepsilon) \\ B(\varepsilon) \end{matrix}\right\} = \frac{1}{2}\left[\frac{F^1(\varepsilon)}{\alpha^1} + \frac{F^2(\varepsilon)}{\alpha^2} \pm \sqrt{\left(\frac{F^1(\varepsilon)}{\alpha^1} - \frac{F^2(\varepsilon)}{\alpha^2}\right)^2 + \frac{4|\Delta|^2}{\alpha^1\alpha^2}}\right], \quad (27)$$

3.3. Ground state energy

Also the energy E of the ground state can be expressed in terms of $G(\omega)$. From (4) and (25) it follows (with $T \to 0$)

$$E = \langle H \rangle = -\frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\varepsilon_F} d\omega \sum_{\underline{k}\sigma\nu} \left[\varepsilon_{\underline{k}}^\nu + \frac{U^\nu \frac{n^\nu}{4}(\omega - \omega_0 \delta_{\gamma_2})}{\omega - \omega_0 \delta_{\gamma_2} - U^\nu(1 - \frac{n^\nu}{2})} + \frac{|\Delta_{\underline{k}}|^2}{F^{\bar\nu}(\omega) - \varepsilon_{\underline{k}}^{\bar\nu}}\right] G_{\underline{k}\sigma}^{\nu\nu}(\omega) \quad (28)$$

In the same way as for $D^\nu(\varepsilon)$ one obtains

$$\frac{E}{N} = 2 \sum_\nu \alpha^\nu A^\nu \int_{-\infty}^{\varepsilon_F} d\omega \, \frac{Z_1^\nu(\omega) f(\alpha^\nu A(\omega), w^\nu) + Z_2^\nu(\omega) f(\alpha^\nu B(\omega), w^\nu)}{A(\omega) - B(\omega)} \quad (29)$$

where

$$Z_1^\nu(\omega) = \left(A(\omega) + \frac{U^\nu n^\nu/4}{\omega - \omega_0 \delta_{\gamma_2} - U^\nu} \cdot \frac{F^\nu(\omega)}{\alpha^\nu}\right)\left(\frac{F^\nu(\omega)}{\alpha^\nu} - B(\omega)\right) - \frac{|\Delta|^2}{\alpha^1\alpha^2}$$
$$Z_2^\nu(\omega) = \left(B(\omega) + \frac{U^\nu n^\nu/4}{\omega - \omega_0 \delta_{\gamma_2} - U^\nu} \cdot \frac{F^\nu(\omega)}{\alpha^\nu}\right)\left(\frac{F^\nu(\omega)}{\alpha^\nu} - A(\omega)\right) - \frac{|\Delta|^2}{\alpha^1\alpha^2} \quad (30)$$

The Fermi energy ε_F is defined by

$$n \overset{!}{=} \sum_\nu n^\nu A^\nu, \qquad n^\nu = 2 \int_{-\infty}^{\varepsilon_F} d\omega \, D^\nu(\omega)/A^\nu. \quad (31)$$

Since in (24) the $F^\nu(\omega)$ depend on n^ν , a coupled system of equations for ε_F , n^ν , and $D^\nu(\varepsilon)$ follows, which can be solved self-consistently. If this is done, E can be caloulated by the integral (29).

4. Metal-insulator transition

4.1. Criterion for stability

From the known condition for thermodynamic stability

$$\left.\frac{\partial F}{\partial p}\right|_T = -V, \qquad \left.\frac{\partial V}{\partial p}\right|_T < 0 \quad (32)$$

it follows, that the second derivation of the free energy F in dependence on pressure must be positive. Hence if a region exists where

$$\left.\frac{\partial^2 F}{\partial p^2}\right|_T < 0, \quad (33)$$

then this region is instable, and a transition takes place from a volume v_1 to a volume v_2, both belonging to the same pressure p. Such a transition is always connected with the appearance of hysteresis.

For the model (4), without interaction between lattice and electronic system,

$$F = F_{\text{lattice}} + F_{\text{electron}} . \qquad (34)$$

Since only phase transitions are considered, which are caused by the electron-electron correlation, it can be assumed, that in F_{lattice} no anomalies exist. Hence (see e.g. Weller 1972)

$$\frac{\partial^2 F_{lattice}}{\partial p^2}\Big|_T = \varkappa_1 v , \quad \varkappa_1 > 0 . \qquad (35)$$

Herein $\varkappa_1$ is the (hypothetical) compressibility of the lattice with fixed electronic system. The electronic system is considered at $T = 0$, hence $F_{\text{electron}} = E$ with E from (29). Therefore the condition for the appearance of such a phase transition is

$$\frac{\partial^2 (E/N)}{\partial p^2} + \varkappa_1 v_0 < 0 , \qquad (36)$$

where $v_0 = V/N$.

In (29) the parameters depending on pressure are w^ν, U^ν, and Δ. It is suitable to relate all these values to the band width w and to discuss the proportionality of E to w separately. With (18) one obtains

$$\left[1 - (1 - \frac{\gamma_u}{\gamma_w}) \sum_\nu u^\nu \frac{\partial}{\partial u^\nu}\right]^2 \left(\frac{E}{Nw}\right) + \frac{\varkappa_1 v_0}{\gamma_w^2 \varkappa_0^2 w} < 0 , \qquad (37)$$

where only the dependence of the energy on the U^ν occurs.

4.2. Qualitative behaviour

The behaviour of the density of states in the case $\Delta = 0$ is plotted in fig.1, assuming a parabolic band

$$f(\varepsilon, w) = \frac{2}{\pi w^2} \sqrt{w^2 - \varepsilon^2}\ \theta(w - |\varepsilon|) . \qquad (38)$$

($\theta(x)$ is a step function.) Of course the qualitative results are independent of this particular form.

Fig.1a. shows the density of states for $c = 0$ without electron-electron interaction $(U^\nu = 0)$. In fig.1.b. the splitting in the subbands $\nu = 1$ and $\nu = 2$ is plotted $(c \neq 0,\ U^\nu = 0)$. Finally fig.1.c. shows the splitting caused by the electron-electron correlation $(U^\nu \neq 0)$, where each subband once more splits into upper $(1u, 2u)$ and lower $(1l, 2l)$ subband. If the original band was half-filled, the Fermi energy lies in the gap, hence the system has the properties of an insulator or semiconductor $(D(\varepsilon_F) = 0)$.

Changing U^ν, the $2u$-subband moves through the gap of the band 1. Thereby the Fermi energy ε_F moves from the gap into the lower subband $1l$ (fig.2), hence the system becomes a metal $(D(\varepsilon_F) \neq 0)$. But with $\Delta = 0$ this transition causes a continuous change of ε_F. The width of the gap, that means the difference between the lower bound of $2u$ and the upper bound of $1l$, can be used as "small parameter" in the sense of Landau's theory of phase transitions. Therefore this phase transition is of second order, without a jump in the conductivity. Now the influence of the hybridization $(\Delta \neq 0)$ will be discussed. If the subbands 2 lie in the centres of 1, these effects are rather small. This is not the case at the edges of the bands, that means in the region

$$U^{(2)} + \omega_0 \approx U^{(1)}\,(1 - n^\nu/2), \qquad (39)$$

corresponding to the region of the expected phase transition. Here the hybridization effects a strong change of the density of states, for instance the appearance of additional small gaps, and therefore an essentially changed dependence of the Fermi energy on the U^ν. A "small parameter" does not exist, in contradiction to the case $\Delta = 0$. Hence in the case $\Delta \neq 0$ a jump of the conductivity can be expected, caused by the mentioned instable region. Weller (1972) considered a similar situation. He discusses the disappearance of the gap in the usual s-band model (1), likewise resulting a shift of ε_F. By the change of the form of the density of states at the band edges, this shift also shows discontinuities, caused by the existence of a thermodynamically instable region (33). However the manner of the disappearance of the gap depends on the used approximations, influencing therefore the type of the resulting phase transition. Such a dependence does not exist in the present paper, since it is only assumed, that generally gaps exist, which is certainly right at large U^ν (Harris and Lange 1967). Essentially, changes of the form at the band edges are only caused by the hybridization, which is completely taken into account.

Altogether these qualitative considerations show, that in the strongly hybridizied two-band model a phase transition

can occur, connected with a jump of the conductivity. Thereby hysteresis effects are mainly caused by the jump of the volume, obtained simultaneously.

4.3. Numerical results

The qualitative discussions of the subsection 4.2 will be completed by some quantitative considerations. For that the dependence of the ground state energy E on the U^ν is studied in the region (39).

The strongest change of ε_F appears, if U^2 essentially stronger depends on p than U^1. Therefore it is sufficient to study only the case of the same dependence on pressure of both U^ν. If already in this case the condition (37) for appearance of an instable region can be fulfilled, then this is possible also for other relations between the U^ν. In consequence of (18) it is improbable, the U^2 weaker depends on p than U^1.

In fig.3. the behaviour of E versus $U\,(=U^1=U^2)$ is plotted for different values of Δ. Fig.3. shows also

$$F(U) = \left(1 - \frac{3}{2} U \frac{\partial}{\partial U} + U^2 \frac{\partial^2}{\partial U^2}\right)(E/Nw), \qquad (40)$$

which corresponds to the first term of (37) in the case $U^1 = U^2 = U$. In agreement with the qualitative considerations $F(U)$ is strongly negative for larger Δ. Therefore it is possible to fulfill the equation (37) for appropriate combinations of the parameters.

To study quantitatively the behaviour of $V0$, the band width w can be obtained from theoretically calculated densities of states (Tewari 1972, Heine and Mattheiss 1971) with $w \sim 0.45\ Ry$. v_0 is given by the lattice parameter $a = 4.1\ \text{Å}$ (Adler 1968). For $\varkappa_0$ and $\varkappa_1$ experimental values are not known. Therefore the value $\varkappa_0 \approx 5 \cdot 10^{-12}\ dyn^{-1}\ cm^2$, valid for similar systems (Leibfried 1955), is used. The same value is assumed for $\varkappa_1$. With these parameters the condition (37) is really fulfilled for sufficiently large hybridization ($\Delta > 0.9w$, see fig.3c).

From (39) it is possible to caloulate the critical pressure p_M for the metal-insulator transition. With (18), $U^1 \approx U^2$, and ω_0 and U^1 from experimentally observed densities of states (Goodenough 1972) it follows

$$p_M = -\frac{1}{(\gamma_w - \gamma_u)\varkappa_0} \ln\left(\frac{2|\omega_0|}{U^1}\Big|_{p=0}\right) \approx \frac{0.672}{\varkappa_0}. \qquad (41)$$

Using $\varkappa_c \approx 5 \cdot 10^{-12}\,dyn^{-1}cm^2$ (at $p=0$) and

$\partial \varkappa_c / \partial p \approx 4\,\varkappa_c^2$ (Leibfried 1955) $p_M \approx 35$ kbar

follows. With $\partial T_M / \partial p \approx -3\,°K/kbar$ (Austin 1962)

a transition temperature of $T_M \approx 100°K$ (at $p=0$)

is obtained. This result surprisingly well agrees with the value $T_M = 126°K$ obtained by some measurements (Morin 1959, Warren et.al. 1967, Austin 1962).

5. Conclusions:

For the two-band Hubbard-model (4) the possibility of a phase transition from an insulator to a metal is proved, as well by qualitative considerations as by numerical calculations. This transition shows some analogies to the Lifshitz-instabilities, and it is connected with a change of volume at the transition point. Thereby hysteresis and jump of the conductivity are caused.

Simultaneously it is shown, that the model (4) describes some properties of the system VO with 16% vacancies. Hence by these theoretical considerations it can be proposed, that in this system a metal-insulator transition occurs, although the experimental results are not completely evident.

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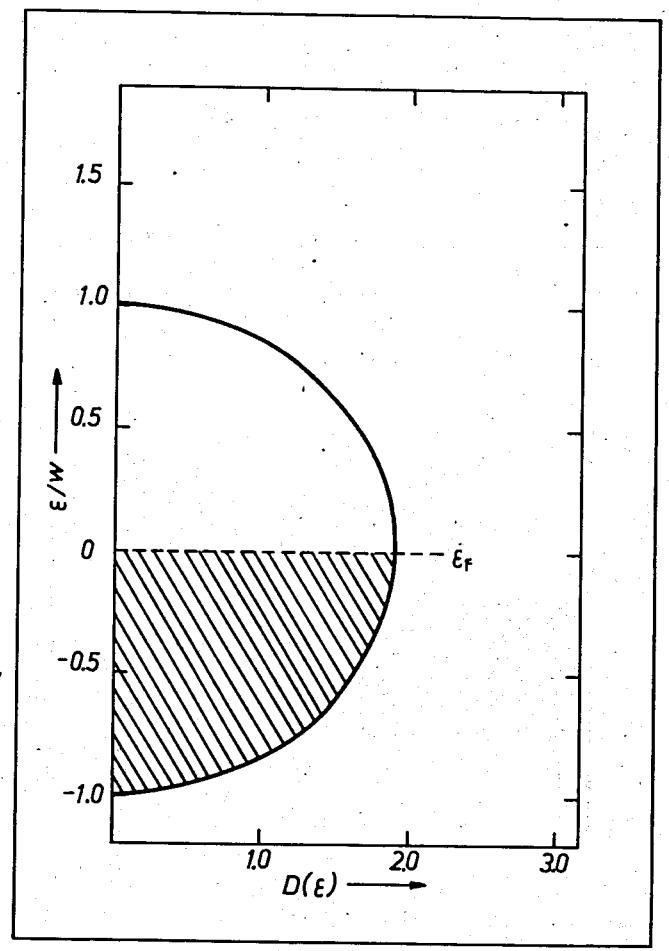

Fig.1. Behaviour of the density of states at $\Delta = 0$.
a) $c = 0$, $U' = 0$.

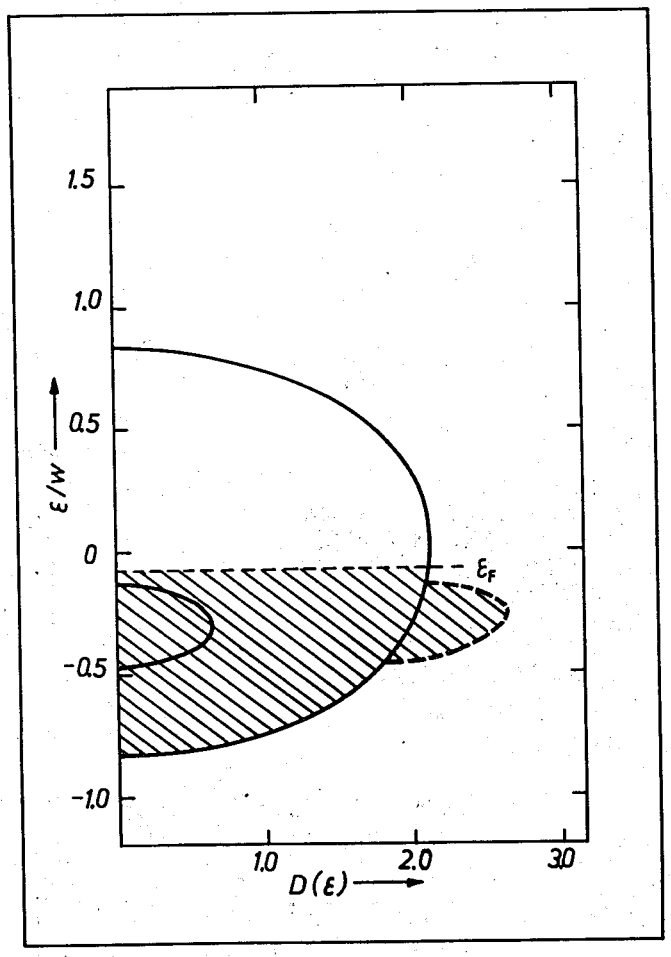

Fig. 1. Behaviour of the density of states at $\Delta = 0$.

b) $c = 0.16$, $U' = 0$, $\omega_c = -0.30W$.

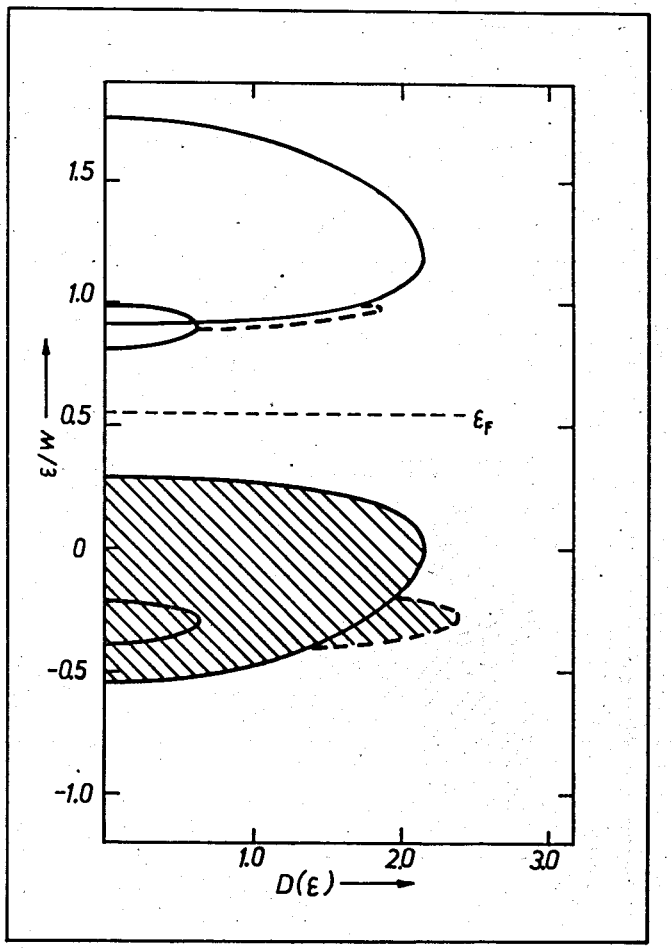

Fig. 1. Behaviour of the density of states at $\Delta = 0$.

a) $c = 0.16$, $U' = 1.20W$, $\omega_c = -0.30W$.

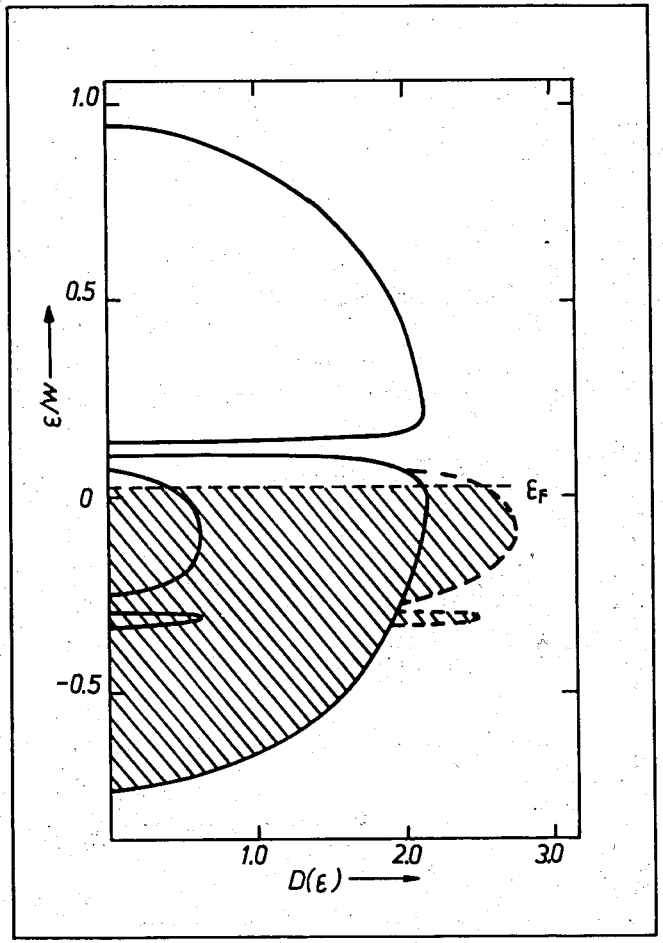

Fig.2. Density of states at larger p .
($\Delta = 0$, $c = 0.16$, $U^* = 0.20w$, $\omega_s = -0.30w$)

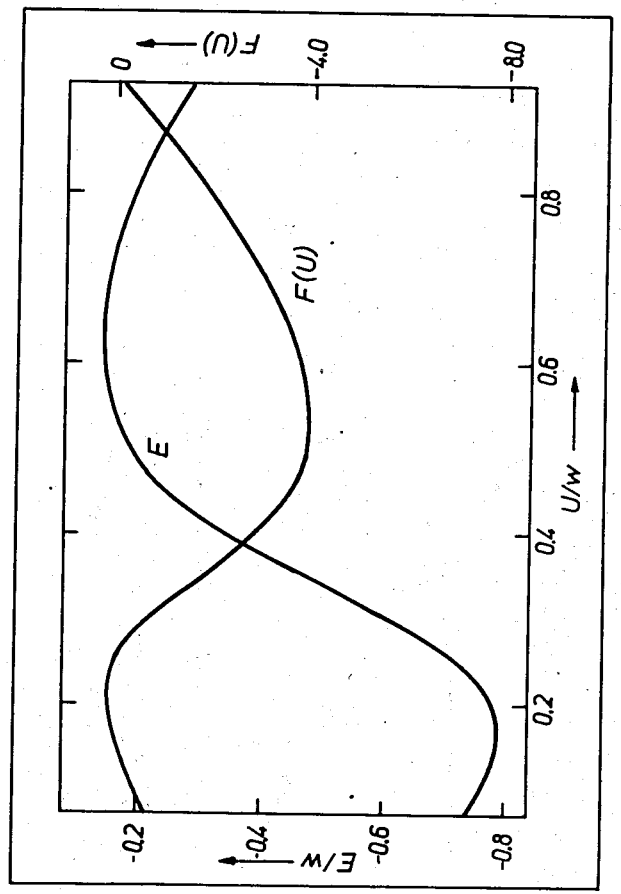

Fig.3. Behaviour of the energy E and $F(U)$ versus U .
a) $\Delta = c$.

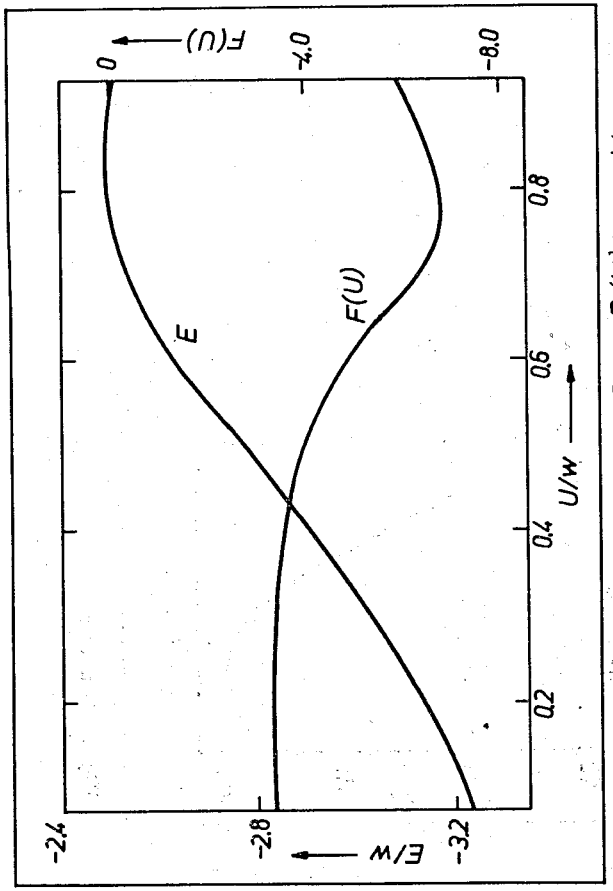

Fig. 3. Behaviour of the energy E and $F(U)$ versus U.
b) $\Delta = w$.

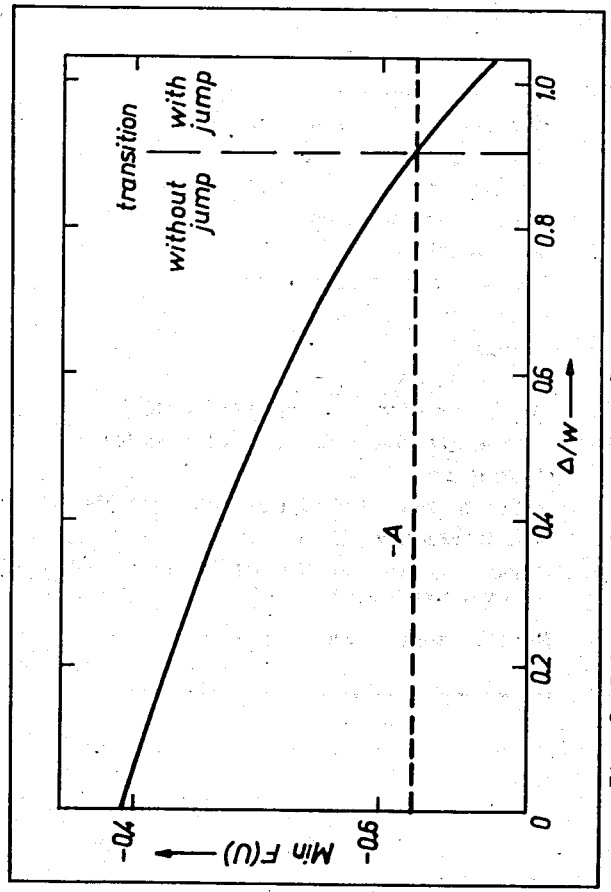

Fig. 3. Behaviour of the energy E and $F(U)$ versus U.
a) Shift of Min F(U) versus Δ.
(A is the second term of eq. (37)).