The Hubbard model for the transition metals and the anomalies in their specific heat and magnetic susceptibility

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The Hamiltonian of the Hubbard model is written down in the representation of many-electron operators. General formulas connecting the usual Fermi operators and the many-electron operators are proposed. Degenerate d^1 and d^2 configurations are specifically investigated. The spectrum obtained consists of a number of bands corresponding to the atomic terms, and for even the d^n configuration the bands arising from ^1L singlet terms may be extremely narrow (localized levels). The proposed model enables us to explain qualitatively the relatively low value of the specific heat for elements with an even number of d electrons per atom, and also explains the strong temperature dependence of their paramagnetic susceptibility.

Up till now the theory of the transition metals has faced substantial difficulties. The reason for this state of affairs is the necessity to simultaneously take into account the strong interaction between the electrons and the periodic lattice potential. Such a calculation can be accomplished within the framework of the Hubbard model.[1-3] However, its extension to the case of degenerate electron configurations (of the type d^n) turns out to be extremely cumbersome. The application of the many-electron operator technique is more effective here. One of the possible types of such operators (transition operators) was proposed by Hubbard[4] and used in[5] to investigate the magnetic properties of a system of d-electrons in a crystal in the simplest case. The electrical properties of the d-electrons were investigated in article[6] in an analogous situation by applying the second-quantization operators which correspond to many-electron wave functions of the atomic type.[7] The introduction of these operators enables us to determine the connection between the Hubbard operators and the ordinary single-electron Fermi operators,[8] this relation being essential for the construction of a general technique.

In the present article we consider a general scheme for obtaining the Hamiltonian of a system of d-electrons in a crystal in the representation of many-electron operators, including the calculation of the coefficients in terms of single-electron matrix elements. The d^1 and d^2 configurations will be specifically considered with the lowest and first-excited Coulomb terms (^2D, ^3F, ^1D, ^4F) taken into consideration. The latter is quite essential for the transition metals, where the separation between terms is comparable with the magnitude of the crystal potential. The spectrum obtained reveals certain characteristic features for each configuration, and these can be used to elucidate the distinctive features of the observed properties of the transition metals.

1. THE HAMILTONIAN IN THE REPRESENTATION OF MANY-ELECTRON OPERATORS AND THE EQUATIONS FOR THE GREEN'S FUNCTIONS

The case of s-electrons was investigated by the author earlier.[8] In the general case the transition from the usual second-quantized representation to the many-electron operator representation $X(\Gamma_n\Gamma_n'{}')$ ($\Gamma = S\,L\,\mu\,M$), where S and L denote the magnitudes of the total spin and orbital angular momentum of the l^n configuration of n electrons and μ and M are their projections, is accomplished by the following formulas (see Appendix 1, p = 2(2l + 1))

$$a_\gamma{}^+=\sum_{n=1}^{\nu}\sum_{\Gamma_n\Gamma_{n-1}}\sqrt{n}\,G_{\Gamma_{n-1}}^{\Gamma_n}C_{\gamma,\Gamma_{n-1}}^{\Gamma_n}X(\Gamma_n\Gamma_{n-1}). \tag{1}$$

Here $G_{\Gamma_{n-1}}^{\Gamma_n}$ are the Racah parentage coefficients, and for the case of LS coupling one has[9]

$$C_{\gamma,\Gamma_{n-1}}^{\Gamma_n}\equiv C_{1/2\sigma,S_{n-1}\mu_{n-1}}^{S_n\mu_n}C_{lm,L_{n-1}M_{n-1}}^{L_nM_n}.$$

Relation (1) can be derived by calculating the matrix elements of the operators a_γ^+ in the representation Γ_n, where the latter can be written in the form $|\,\Gamma_n\rangle = A_{\Gamma_n}^+|\,0\,\rangle$, where $A_{\Gamma_n}^+$ is the many-electron second-quantization operator introduced in[7], which is a linear combination of produce of the n operators a_γ^+.

One can easily verify with the aid of (1) that the anti-commutation rules for a_γ are indeed satisfied if the operators $X(\Gamma_n\Gamma_n'{}')$ satisfy the Hubbard multiplication rules[4] and normalization conditions,

$$[a_\gamma{}^+, a_{\gamma'}]_+=\delta_{\gamma\gamma'}\sum_{n\Gamma_n}X(\Gamma_n)=\delta_{\gamma\gamma'},\quad X(\Gamma_n)\equiv X(\Gamma_n\Gamma_n). \tag{2}$$

With the aid of (1) the Hubbard Hamiltonian (the Coulomb interaction between n_ν electrons at site ν is taken into account) takes the form ($\{\Gamma_n\}\equiv\Gamma_n^{(1)}\Gamma_n^{(2)}\ldots$; $\{i\}\equiv i_1\ldots i_p$)

$$\begin{aligned}\hat{\mathscr{H}}=&\sum_{\nu n\{\Gamma_n\}\{i\}}\left[n_\nu\varepsilon_\nu+\frac{1}{2}n_\nu(n_\nu-1)Q_\nu{}^l(\Gamma_n)\right]X_\nu(\Gamma_n)\hat{\Phi}(i_1\ldots i_n-1\ldots i_p)\\ &+\sum_{\nu_1\neq\nu_2n_1n_2\{\Gamma\}\{i\}}B(\nu_1\Gamma_{n_1},\nu_2\Gamma_{n_2-1};\nu_1\Gamma_{n_1-1}\nu_2\Gamma_{n_2})\\ &\times X_{\nu_1}(\Gamma_{n_1}\Gamma_{n_1-1})\hat{\Phi}(\ldots i_{n_1-1}-1\ldots i_{n_2}-1\ldots)X_{\nu_2}(\Gamma_{n_2-1},\Gamma_{n_2}).\end{aligned} \tag{3}$$

In contrast to previous work, we obtain here in the general case explicit expressions for Q_ν and $B(\nu\Gamma,\ldots)$ in terms of the single-electron matrix elements of the Coulomb interaction and of the lattice potential (see Appendix 2).

In addition, in analogy to[8], in expression (3) are conserved the diagonal operator products

$$\hat{\Phi}(i_1\ldots i_p)=(i_1!\ldots i_p!)^{-1}\sum_{\{\nu_1\}\ldots\{\nu_p\}}\prod_{\nu_1=1}^{i_1}X_{\nu_1}(\Gamma_1)\ldots\prod_{\nu_p}^{i_p}X_{\nu_p}(\Gamma_p), \tag{4}$$

which take into account, in the representation of second quantization, the restrictions imposed in the summation over sites by the Pauli correlations ($i_1\ldots i_p$ denote

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the number of sites with configurations $l^1 \ldots l^p$).

Expression (3) has an important advantage over the usual representation, namely, the Coulomb interaction is diagonal. To be sure, if the crystalline potential is comparable with the Coulomb interaction, then we must also investigate the matrix elements B(...) which are off-diagonal in Γ, including the excited states Γ_n. However, this problem is solvable if we limit ourselves to the first excited terms. This limitation apparently corresponds qualitatively to the actual situation in transition metals. As we shall see later on, equations of the Slater-Koster type[10] are obtained in the limiting case as Q → 0, these being characteristic of the tight-binding approximation. This implies that the scheme described in the present article is valid in both limiting cases. It is natural to anticipate that for Q ≈ B we shall have some kind of interpolation that describes approximately the actual situation.

We shall carry out the subsequent calculations by using the Green's function method. We introduce the equal time retarded temperature Green's function

$$G_{\nu\nu'}(\Gamma_{n-1}\Gamma_n|\Gamma'_{n'}\Gamma'_{n'-1}) = \langle\langle X_\nu(\Gamma_{n-1}\Gamma_n)|X_{\nu'}(\Gamma'_{n'}\Gamma'_{n'-1})\rangle\rangle.$$

The equation of motion with the Hamiltonian (3) takes the form (N is the number of sites)

$$EG_{\nu\nu'}(\Gamma_{n-1}\Gamma_n|\Gamma'_{n'}\Gamma'_{n'-1}) = \frac{1}{2\pi}\langle[X_\nu(\Gamma_{n-1}\Gamma_n), X_{\nu'}(\Gamma'_{n'}\Gamma'_{n'-1})]_+\rangle + \langle\langle[X_\nu(\Gamma_n\Gamma_{n-1}), \hat{\mathscr{H}}]_-|X_{\nu'}(\Gamma'_{n'}\Gamma'_{n'-1})\rangle\rangle, \quad \nu,\nu'=1\ldots N. \tag{5}$$

Let us substitute $\hat{\mathscr{H}}$ from (3) into (5) and then decouple the operators belonging to different sites. Since the commutators $[X_\nu, \hat{\Phi}]_-$ obtained after the substitution always contain an off-diagonal operator of the type $X_\nu(\Gamma_{n-1}, \Gamma_n)$ with $\nu \neq \nu_1, \nu_2$, the corresponding Green's functions will vanish provided that

$$\overline{X_\nu(\Gamma_n\Gamma_{n'})} = 0, \quad \Gamma_n \neq \Gamma_{n'}. \tag{6}$$

Then instead of Eq. (5) we obtain (N′ = N − 1, N − 2)

$$\begin{aligned}&[E - E(\Gamma_n)\overline{\Phi_{N-1}(\ldots i_n - 1)} + E(\Gamma_{n-1})\overline{\Phi_{N-1}(\ldots i_{n-1}-1\ldots)}]\\ &\times G_{\nu\nu'}(\Gamma_{n-1}\Gamma_n|\Gamma'_{n'}\Gamma'_{n'-1}) = \{\overline{X(\Gamma_n)} + \overline{X(\Gamma_{n-1})}\}\Big[\frac{1}{2\pi}\delta_{\nu\nu'}\delta_{\Gamma_n\Gamma'_{n'}}, \delta_{\Gamma_{n-1}\Gamma'_{n'-1}}\\ &+\overline{\Phi_{N'}(\ldots)}\sum_{\nu_2(\neq\nu)n_2\Gamma''_{n_2}\Gamma''_{n_2-1}} B(\nu\Gamma_n, \nu_2\Gamma''_{n_2-1}; \nu\Gamma_{n-1}, \nu_2\Gamma''_{n_2})\\ &\times G_{\nu_2\nu'}(\Gamma''_{n_2-1}\Gamma''_{n_2}|\Gamma'_{n'}\Gamma'_{n'-1})\Big].\end{aligned} \tag{7}$$

Now let us proceed to the discussion of specific electron configurations.

2. THE CONFIGURATION d^1

First let us consider the simplest case of the d^1 configuration. To allow for processes involving the creation and annihilation of holes and pairs, it is necessary to take the neighboring configurations d^0 and d^2 into consideration. The remaining configurations d^n (with n > 2) lie higher and do not play an important role. Taking only the lowest Hund term ^3F for the d^2 configuration into account and changing to the Fourier transform $G_k(\Gamma_n\Gamma_{n'})$, we obtain the following result (n = 1, 2) from Eq. (7):

$$\begin{aligned}&[E - \varepsilon_d\overline{\Phi_{N-1}(\ldots i_d - 1\ldots)} + \varepsilon_0\overline{\Phi_{N-1}(\ldots i_0-1\ldots)} - \tilde{B}_k(d00d)]G_k(0d|d0)\\ &= \frac{\overline{X(d)}+\overline{X(0)}}{2\pi N} + \sum_{d'(\neq d)}\tilde{B}_k(d00d')G_k(0d'|d0) + \sum_{d'\Gamma_2}\tilde{B}_k(dd'0\Gamma_2)G_k(d'\Gamma_2|d0),\end{aligned} \tag{8}$$

$$\begin{aligned}&[E - E_{\Gamma_2}\overline{\Phi_{N-1}(\ldots i_2 - 1\ldots)} + \varepsilon_d\overline{\Phi_{N-1}(\ldots i_d-1\ldots)} - \tilde{B}_k(\Gamma_2 d\, d\Gamma_2)]G_k(d\Gamma_2|\Gamma_2 d)\\ &= \frac{\overline{X(\Gamma_2)}+\overline{X(d)}}{2\pi N} + \sum_{d'\Gamma_2'(\neq d\Gamma_2)}\tilde{B}_k(\Gamma_2 d'\, d\Gamma_2)G_k(d'\Gamma_2'|\Gamma_2 d)\\ &+ \sum_{d'}\tilde{B}_k(\Gamma_2 0 dd')G_k(0d'|\Gamma_2 d),\end{aligned} \tag{9}$$

where the Fourier components of the transfer matrix elements are given by

$$\tilde{B}_k(\Gamma_{n_1}, \Gamma'_{n_2-1}; \Gamma_{n_1-1}, \Gamma'_{n_2}) = \{\overline{X}(\Gamma_{n_1-1}) + \overline{X(\Gamma'_{n_2-1})}\}\overline{\Phi}_{N'}B_k(\Gamma_{n_1}, \Gamma'_{n_2-1}; \Gamma_{n_1-1}, \Gamma'_{n_2}), \tag{10}$$

and we are using the symbols 0, d, and Γ_2 to denote the states d^0, $d^1(^2D)$, and $d^2(^3F)$.

We can write down similar equations for the new type Green's functions $G_k(d'\Gamma_2|d\,0)$ and $G_k(0\,d'|\Gamma_2 d)$ which appear on the right sides of Eqs. (8) and (9); these new equations differ from (8) and (9) by the absence of the inhomogeneous terms. Then we obtain the complete system of equations for G_k. Setting the determinant of this system of equations equal to zero corresponds to the condition for the existence of poles in the Green's function, i.e., it yields the equation for the determination of the quasiparticle spectrum:

$$\mathrm{Det}|(E - E_{\Gamma_n} + E_{\Gamma_{n-1}})\delta_{\alpha\beta} - \tilde{B}_{\alpha\beta}| = 0, \quad n=1, 2, \tag{11}$$

the subscripts α and β label the rows and columns of the determinant and in our case take the values 0, d, and ^3F (S = 1, L = 1, μ, M).

One can easily verify that by neglecting creation and annihilation processes (which corresponds to going over to a single-configuration approximation), we obtain from Eq. (11) the well known equations of the Slater-Koster type[10] (tight-binding approximation) for the d-electrons with allowance for the correlation effects, which are manifest in the appearance of the factors

$$\overline{\{\overline{X(\Gamma_n)} + \overline{X(\Gamma_{n-1})}\}\Phi_N(\ldots)}.$$

Since the quantities $\overline{X(\Gamma_n)}$ can be expressed in terms of the Green's functions, which in turn are expressed in terms of $X(\Gamma_n)$, one can obtain for the determination of $\overline{X(\Gamma_n)}$ a closed system of equations, which is supplemented by the normalization conditions ($\bar{n}$ denotes the average number of electrons per site):

$$\sum_n \overline{X(\Gamma_n)} = 1, \quad \sum_n n\overline{X(\Gamma_n)} = \bar{n}. \tag{12}$$

Thus, these equations make it possible for us to calculate the spectrum, density of states, etc. in a certain kind of interpolation scheme between the conventional tight-binding approximation (Q = 0) and the case corresponding to the atomic limit (B → 0). We shall not carry out here any further calculations for the d^1 configuration, which turns out to have a complicated spectrum of overlapping bands, but instead let us go on to investigate the d^2 configuration since, as will become clear, the possibility of a qualitative comparison of these two cases exists (without detailed calculations), and such a comparison leads to a number of interesting conclusions.

3. THE CONFIGURATION d^2

In calculating the spectrum of the d^2 configuration, significant differences show up in comparison with the d^1 case. As is well known, the excited terms ^1D, ^3P, ^1G, and ^1S of the d^2 configuration lie rather close to the ground term ^3F (for example, $E(^1D) - E(^3F) \approx 1$ eV). During the formation of bands in a crystal, these terms may turn out to be located within the lower ^3F band. We must take this fact into account when investigating Eq. (7). For the excited d^1 and d^3 configurations we shall accordingly consider only the ground terms ^2D and ^4F. Consideration of Eq. (7) again leads to an equation for the determination of the energy spectrum, of the type (11) with n - 2, 3. Equation (11) breaks up into a series of independent equations according to the symmetry of the coefficients $\tilde{B}_{\alpha\beta}$.

Let us consider Eq. (7) for the states of the singlet terms of the type ^1L $(= {}^1D, {}^1G, {}^1S)$:

$$\begin{gathered}[E-E(^1L)\overline{\Phi_{N-1}(i_2-1)}+\varepsilon_d\overline{\Phi_{N-1}(i_1-1)}]G_{\nu\nu'}(d^1L|^1Ld)=\frac{1}{2\pi}\delta_{\nu\nu'}[\overline{X(^1L)}\\ +\overline{X(d)}]+[\overline{X(^1L)}+\overline{X(d)}]\sum_{\nu_2(\neq\nu)}\Big\{\sum_{d''\Gamma_2''}B(\nu^1L,\nu_2d'';\nu d,\nu_2\Gamma_2'')\\ \times\overline{\Phi_{N-2}(i_1-1,i_{1L}-1)}G_{\nu_2\nu'}(d''\Gamma_2''|^1Ld)+\sum_{\Gamma_2''\Gamma_3''}B(\nu^1L,\nu_2\Gamma_2'';\nu d,\nu_2\Gamma_3'')\\ \times\overline{\Phi_{N-2}(i_2-2)}G_{\nu_2\nu'}(\Gamma_2''\Gamma_3''|^1Ld)\Big\}.\end{gathered}\tag{13}$$

Here $d = m\sigma$, $^1L = 0L0M_1$, $\Gamma_2'' = {}^3F{}^1L(\mu_2M_2)$, and $\Gamma_3'' = {}^4F(3/2, 3, \mu_3M_3)$. It is clear from Eq. (13) that the terms corresponding to the creation or annihilation of the excited states d and $d^3(^4F)$ due to the transfer of an electron between sites must, generally speaking, satisfy the conditions for conservation of angular momentum—both spin and orbital angular momentum. Thus, for example, the transition of two sites from the states $^1L^1L(S = 0)$ into the states d and $d^3(^4F)$ $(S \neq 0)$ is associated with nonconservation of the total spin. The situation is somewhat more complicated with regard to transitions of the type $d^2(^1L) + d^2(^3F) \to d^1(^2D) + d^3(^4F)$ $(S = 0 + 1 \to 3/2 \pm 1/2)$ since states having $S = 1$ also exist among the final states. However, in the first place it is necessary to recognize that such transitions occur as a result of the interaction of different terms (^1L and ^3F). In the second place, after taking account of the crystalline field in ^1L and of the partial lifting of the orbital degeneracy, similar prohibitions can also arise with respect to the orbital quantum numbers, as a more detailed analysis shows. (In particular, such a situation occurs for the orbital singlets $^1\Gamma_1$ which are obtained from the ^1L terms, whereas for the ^3F and ^4F terms the doublet states turn out to be the lowest.)

Conversely, no selection rules at all appear for the processes $^1L + {}^3F \to {}^3F + {}^1L$. The latter thus specify the dispersion part of the ^1L-band spectrum, while the creation and annihilation processes that are forbidden by the selection rules for the ^1L states do not play any role. Omitting the corresponding terms in Eq. (13), we obtain the spectrum of the singlet states in the form

$$E=E(^1L)-\varepsilon(d)+\sum_{d'',\Gamma_2''={}^1L,{}^3F}\tilde{B}_{\mathbf{k}}(^1Ld'',d\Gamma_2'').\tag{14}$$

At the same time, for the states of the ground term $d^2(^3F)$ the creation and annihilation processes satisfy the S and L conservation laws ($^3F + {}^3F = {}^2D + {}^4F$; $S = 1 + 1 = 1/2 + 3/2$) and, therefore, these processes must be retained in the equations. In this case[1] we obtain the following set of equations from the general equation (7):

$$\begin{gathered}(E-\varepsilon_2)G_{22}+b_{0'2}G_{0'2}+b_{23}G_{32}=a_2,\\ b_{20'}G_{22}+(E-\varepsilon_{0'})G_{0'2}+b_{30'}G_{32}=0,\end{gathered}\tag{15}$$

where the following abbreviations have been introduced: the symbol 0′ corresponds to the ^1L term, 2 corresponds to the ^3F term, and 3 to $^4F(d^3)$, so that

$$\begin{gathered}\varepsilon_2=E_2-\varepsilon_d+b_{22},\quad a_2=[\overline{X(d)}+\overline{X(2)}]/2\pi N,\\ b_{22}=[\overline{X(d)}+\overline{X(2)}]\overline{\Phi_{N-1}(i_2-1,\ i_3)}B_{\mathbf{k}}(2dd2),\\ b_{0'2}=-[\overline{X(d)}+\overline{X(2)}]\overline{\Phi_{N-1}(i_2-1,\ i_3)}B_{\mathbf{k}}(2dd0'),\\ b_{20'}=-[\overline{X(0')}+\overline{X(d)}]\overline{\Phi_{N-1}(i_{0'}-1,\ i_3)}B_{\mathbf{k}}(0'dd2)\end{gathered}\tag{16}$$

and so forth.

An estimate of the average values of Φ (see Appendix 3) enables us to classify all the matrix elements $b_{\alpha\beta}$ according to the parameter $\overline{X(d)}$. Since in our model $\overline{X(d)}$ $(= \overline{X(3)})$ is the number of quasiparticles in the state due to the increase of the Coulomb energy, one should expect $\overline{X(d)} \ll 1$. Then, by keeping only the largest terms (with respect to this parameter) in Eqs. (15) we obtain the spectrum for the ^3F band in the form

$$\begin{gathered}E(\mathbf{k})={}^1/_2[E(^4F)-\varepsilon_d]\pm{}^1/_2\{[2E(^3F)\\ -\varepsilon_d-E(^4F)]^2+|\tilde{B}_{\mathbf{k}}(^3F,{}^3F;d,{}^4F)|^2\}^{1/2}.\end{gathered}\tag{17}$$

We see that the processes of creation and annihilation, which determine the width of the ^3F band in second order, play the principal role in the dispersion part $\tilde{B}(\mathbf{k})$ of (17).

The physical meaning of this result is that for a small number of d and d^3 configurations the transfer of d^2 states over these configurations is impeded because of their low probability $(\sim\overline{X(d)})$. Therefore, second-order processes give the major contribution $|\tilde{B}_{\mathbf{k}}| \sim \overline{X(d)}^{1/2}$, and such processes require the presence of singly occupied sites only in the final state (including the presence of the X(d)-state, the wave function is $\sim\overline{X(d)}^{1/2}$). To the contrary, for the ^1L band, where the creation and annihilation processes are forbidden, the width depends only on low-probability first-order processes $\sim\overline{X(d)}$.

Rough estimates of $\overline{X(d)}$ can be obtained by calculating the average number of excited states according to the usual formula

$$\overline{X(d)}\approx(\exp(\Delta E/kT)+1)^{-1},$$

where ΔE is the difference, somewhat reduced by the crystalline potential, of the Coulomb energies between the d and d^3 configurations and two d^2 configurations. Assuming, for example, $\Delta E \approx 10^{-13}$ erg we obtain $\overline{X(d)} \approx 10^{-3}$ (for T = 100°K). A more rigorous estimate of $\overline{X(d)}$ must be obtained from the self-consistent equations for the spectral intensity with the Green's functions determined by solving the system (15). The calculations show that in this case the obtained values of $\overline{X(d)}$ are of the same order as the usual values of the parameters for the initial band spectrum. However, the temperature dependence of $\overline{X(d)}$ turns out to be much weaker than for ordinary thermal excitations, owing to the possible existence of a minimum in the energy of the entire system (including the ^3F band of the d^2 configuration, whose width is $\sim\overline{X(d)}^{1/2}$) at definite values $\overline{X(d)} \neq 0$.

Now assuming that the initial width of the band is $\approx B(\mathbf{k}) \approx 3$ eV (a typical value obtained in single-electron calculations) and using formulas (10), (3.4), and (3.5), we obtain for the width of the band, $\Delta_{\mathbf{k}} = E(\mathbf{k}_{\max}) - E(\mathbf{k}_{\min})$, a value ≈ 0.5 eV for the ^3F band (from Eq. (17)) and a value between 10^{-3} and 10^{-2} eV for the ^1L band (from Eq. (14)). Thus, the presence of the factor $\overline{X(d)}$ in the probability for transfer processes and the prohibition of creation and annihilation processes strongly narrows the ^1L band, which leads to the appearance of a sharp maximum in the density of states N(E).

Nevertheless, the cited numerical estimates are only for purposes of illustration. A rigorous calculation can be performed only on the basis of exact wave functions. This can hardly be done for the 3d-metals at the present time, and the same is true for the near future.

Taking into account the atomic-spectroscopy data on the energy positions of the ^3F and ^1L terms ($E(^1D) - E(^3F) \approx 0.8$ eV in Ti), one can estimate that the ^1D term will fall in the ^3F-band in the crystal and, by possessing sufficient capacity, its position will in fact determine the value of the Fermi energy.

This case corresponds to very curious physical properties of a system of d-electrons and can be realized for all even d^n configurations. The experimental data[11,12] point precisely to the existence of regular differences between elements with even and odd ground configurations (see the accompanying figure). Below we shall investigate the electronic specific heat and paramagnetic susceptibility.

4. CALCULATION OF THE ELECTRONIC SPECIFIC HEAT AND PARAMAGNETIC SUSCEPTIBILITY

As is well known, the electronic specific heat c_V and the paramagnetic susceptibility χ of transition metals are appreciably higher than those of nontransition metals; this can be explained by the contribution of the collective d-electrons, which form relatively narrow bands. However, the existing theory does not explain the sharply-expressed alternation in the values of c_V and χ for elements containing even and odd numbers of d-electrons[11] (see the figure), and it also does not explain the strong, almost linear temperature dependence of $\chi(T)$ for elements with a d^2 configuration.[12] The latter cannot be explained by the small term $(kT/E_F)^2$, which is available for the Pauli paramagnetism. Below we shall calculate c_V and χ in the proposed model under certain simplifying assumptions.

The spectrum which is obtained for odd configurations does not differ qualitatively from the usual single-electron calculations except for the fact that the effective width of the band turns out to be narrower, which enables us to explain the enhanced values of c_V and χ which are observed in d^1 (Sc, Y, La) and d^3 (V, Nb, Ta) configurations.[11]

In our model the situation is substantially different for even configurations and can be described by two bands, the width δ of one of these bands (the ^1L-type band) being very small. We consider next the limiting case $kT \gg \delta$, when the quantity δ can be neglected, that is,

$$E_2 = \varepsilon_2 + \beta_2 \cos \mathbf{ak}, \quad E_2' = E_2'(^1L). \tag{18}$$

Calculating the averages $\overline{X}_2$ and $\overline{X}_{2'}$, we have together with the normalization condition (μ denotes the chemical potential)

$$\overline{X}_2 = \frac{1}{6\pi^2} \arccos^3 \frac{\mu - \varepsilon_2}{\beta_2}, \quad \overline{X}_2' = \left[\exp\left(\frac{(E_2' - \mu)}{kT}\right) + 1\right]^{-1}, \qquad \overline{X}_2 + \overline{X}_2' = 1. \tag{19}$$

Here β_2 is to be understood as the effective width of the band, and $\overline{X}_n$ were determined in terms of the Green's function according to the usual formulas

$$G_{\mathbf{k}}(n-1, n | n, n-1) = \frac{1}{2\pi} \frac{\overline{X}_{n-1} + \overline{X}_n}{E - E_n(\mathbf{k})}. \tag{20}$$

From Eqs. (19) we find

$$\mu = E_2' - kT \ln \frac{\overline{X}_2}{1 - \overline{X}_2}. \tag{21}$$

Since $\overline{X}_2$ is a function of μ, Eq. (21) can be regarded as an iterative equation with respect to μ (including $\overline{X}_2 \approx 0$ and 1). Since $kT/E_{2'} \ll 1$, we find $\mu = E_{2'}$ in the first approximation, and in the next approximation μ is linear in T. The physical meaning of (21) is that at for $\overline{X}_2 > 1/2$ (the band is more than half filled) $\mu < E_2'$ and decreases linearly with increasing T (the electrons pass from the band into the level E_2'). To the contrary, if E_2' lies in the lower half, then $\overline{X}_2 < 1/2$, but $\mu > E_2'$ and increases linearly with T (the electrons pass from the level into the band).

Now let us calculate the specific heat of the electron system. The energy of the electrons in the band and in the level is given by

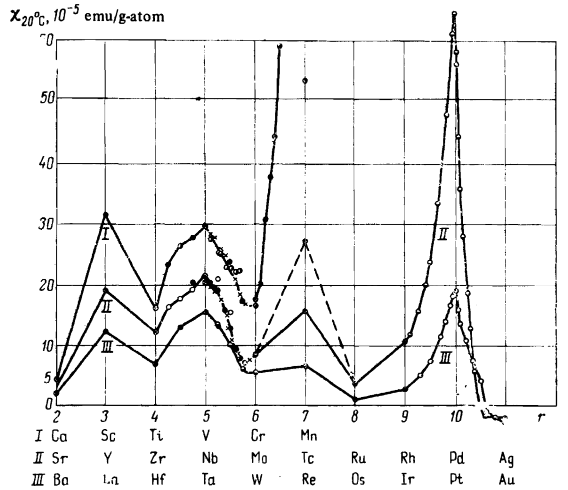
$$u = u_2 + u_2' = u_2 + N\overline{X}_2' E_2', \tag{22}$$

hence, by calculating u_2 and $\overline{X}_2'$ to terms of second order in kT/E_2' we obtain

$$c_v = \left(\frac{\pi^2}{3} + \alpha^2\right) N(E_2') k^2 T = \gamma' T, \quad \alpha = -\ln \frac{\overline{X}_2}{1 - \overline{X}_2}. \tag{23}$$

Expression (23) differs from the usual expression by the presence of the term $\sim\alpha^2$ and by the fact that the density of states N(E) is evaluated at $E = E_2'$, where the Fermi level is now located. The term with α^2 is due to the linear dependence of the chemical potential μ on T, as indicated by Eq. (21). If E_2' does not lie too far from the bottom of the band $E_2(k = 0)$, it is then easy to see that (23) gives a lower value for the specific heat than would be observed in the absence of a local level.

The quantitative results are strongly dependent on the form of the function N(E). For $N(E) = aE^t$ we obtain $\overline{X}_2 \sim E^{t+1}$, whence $N(E) \sim E^t \sim \overline{X}_2^{t/t+1}$; since $\overline{X}_2 = 1$ if no local level is present, the ratio γ'/γ (where γ corresponds to the specific heat of the system without the local level) is given by



Experimental dependence of the paramagnetic susceptibility of transition-metal alloys on the number of electrons according to the review article [11]. The different types of circular symbols correspond to different alloy systems. The quantity r, denoting the number of (d + s)-electrons per atom, is plotted along the axis of abscissas.

$$\frac{\gamma'}{\gamma}=\left(1+\frac{3\alpha^2}{\pi^2}\right)\bar{X}_2^{t/t+1}. \qquad (24)$$

Then for $t = 2$, for example, we obtain $\gamma'/\gamma \approx 0.5$ at $\bar{X}_2 = 0.1$ and $\gamma'/\gamma \approx 0.3$ at $\bar{X}_2 = 0.01$. As is well known from experiment,[11] the ratio of the specific heat (γ') for elements with an even number of electrons (d^2: Ti, Zr, Hf and d^4: Cr, Mo, W) to the specific heat (γ) for elements with an odd number of d-electrons (d^1: Sc, Y, La and d^3: V, Nb, Ta) remains constant over the periodic table, ranging from 0.3 to 0.4, in agreement with our estimates. The latter, of course, are only illustrative in nature; however, the very fact that the elements can be divided into two groups receives a rather clear physical explanation. Elements with an even configuration have singlet levels in the spectrum, giving localized levels against a background of the bands formed by the other d-states. These levels determine the position of the Fermi energy and contain an appreciable fraction of the electrons, which give a contribution to the specific heat only in the case of transitions into the band (the term with α^2 in Eq. (23)). In this connection a substantially smaller number of electrons remains in the normal band, and their density of states at the Fermi level becomes lower, which also leads to a smaller value of c_V. The lower values of c_V in the configurations d^2 and d^4 were previously attributed to the location of the Fermi level at the minimum of the density of states; however, in contrast to the model proposed here, the very fact of the formation of low values of $N(E_F)$ just for the even configurations was purely accidental.

Now let us go on to investigate the paramagnetic susceptibility $\chi(T)$. In the transition metals for all three periods in the configurations d^1—d^4, this quantity obeys the following well expressed relationships:[11,12] 1) the value of χ for even configurations is roughly half as large as for odd configurations; 2) $d\chi/dT > 0$ and is appreciably larger in the even configurations (especially for d^2), while $d\chi/dT \lesssim 0$ and is small in odd configurations; 3) the $\chi(T)$ dependence for even configurations is linear over a wide temperature range (including low temperatures $T < 75°K$).

The explanation of the indicated properties entails serious difficulties from the viewpoint of conventional ideas. The strong temperature dependence of χ for Ti, Zr, and Hf obviously cannot be understood within the framework of the Pauli theory of paramagnetism, where there is only a very small contribution $\sim(kT/\mu)^2$.

In the present model we have (N_A is Avogadro's number and χ is calculated per mole)

$$\chi(T)=N_A\mu_B{}^2N(\mu(T))=N_A\mu_B{}^2N(E_2')\left(1-t\frac{kT}{E_2'}\ln\frac{\bar{X}_2}{1-\bar{X}_2}\right). \qquad (25)$$

Here again, just as in Eq. (24), we assume

$$N(E)=aE^t,\ \frac{dN}{dE}=t\frac{N(E)}{E}, \qquad \bar{X}_2=\int_0^{E_2'}N(E)\,dE=\frac{a}{t+1}E_2'^{\,t+1},$$

from which, at the same estimates as for the specific heat, namely, $t = 2$, $\bar{X}_2 = 0.01$, $E_2' = 2^{-2/3}\beta_2\bar{X}_2^{1/3} \approx (1/5)\beta_2 \approx 10^{-12}$ erg, we obtain

$$\frac{1}{\chi(0)}\frac{d\chi}{dT}=-t\left(\ln\frac{\bar{X}_2}{1-\bar{X}_2}\right)\frac{k}{E_2'}\approx 10^{-3}, \qquad (26)$$

which agrees in order of magnitude with the experimental values for Ti.[12]

The physical reason for such a significant increase of $\chi(T)$ is that when the band is slightly filled, as the temperature increases the electrons pass from the singlet level ${}^1L$ into the band, thus increasing the spin part of χ. Here there is also an orbital contribution from the electrons in the localized levels ${}^1L$. Estimates according to the formula $\chi_{orb} \approx N_A\mu_B^2/3kT$ give a value $\approx 10^{-2}$, which is too high. However, upon taking account of the splitting of the ${}^1L$ levels in the crystal field, the situation essentially depends on the degree of degeneracy of the lowest level which has been split. As the more detailed investigation shows, quenching of the ${}^1L$ levels for the d^2 configuration (the lowest level turns out to be the singlet ${}^1\Gamma_1$) may occur when the influence of the conduction electrons is taken into account. Then only the substantially smaller contribution of the Van Vleck type is left, $\chi_{V\text{-}V} \approx N_A\mu_B^2\bar{X}_2'/\Delta \approx 10^{-4}$, where $\Delta \approx 10^{-12}$ is the magnitude of the splitting. Since this contribution to χ is due to the orbital angular momenta, χ should be strongly anisotropic, as is actually observed experimentally.[12] The indicated mechanism for anisotropy in χ may play a role side by side with the temperature-independent orbital paramagnetism of Kubo and Obata.[13]

Thus, the existence in our model of a very narrow band (or localized levels) in the spectrum of the d-electrons in a crystal, coupled with the presence of low-lying singlet (with respect to spin) terms for even d^n configurations, enables us to qualitatively explain the behavior of the electronic specific heat and the susceptibility of the transition metals.

At the same time the theoretical investigation within the framework of the Hubbard model provides a certain amount of justification for the initial concepts, and it may subsequently serve as the basis for a more detailed quantitative theory. Such a theory may appreciably improve the results of the single-electron calculations, which frequently do not agree among themselves, since it corresponds to a many-configuration approximation, which is extremely important in connection with the investigation of unfilled shells in the transition metals.

APPENDIX 1

Although the transition operators $X(\Gamma_n\Gamma_{n'}')$ were described and used for calculations in[4,5,8], it is useful to explain the physical meaning of these operators and their connection with the second-quantized single-electron operators. $X(\Gamma_n\Gamma_{n'}')$ are the operators which transfer the system of electrons from the state $\Gamma_{n'}'$ into the state Γ_n. If $n' = n - 1$ then such a transition is due to an increase of the number of electrons by unity, i.e., in the single-electron representation it should correspond to the operator a_γ^+ ($\gamma = slm\sigma$, where $s(=1/2)$, l, m, and σ are the single-electron quantum numbers, respectively, of the spin, orbital angular momentum, and their projections). Conversely, if we have a complete set of states Γ_n, the action of the operator a_γ^+ in the space Γ_n is equivalent to all possible transitions $\Gamma_{n-1} \to \Gamma_n$, i.e., it must be described by a linear combination of the operators $X(\Gamma_n\Gamma_{n-1})$.[4]

In contrast to previous articles, in the present article the explicit form of the coefficients in the relationship between a_γ^+ and $X(\Gamma_n\Gamma_{n-1})$ is given for the general case, which allows us to perform concrete calculations for arbitrary states Γ_n.

It is especially easy to visualize the case of s-electrons, for which (according to Eq. (1)) we have

$$a_\sigma^+=(-1)^{1/2-\sigma}X(2,-\sigma)+X(\sigma,0), \tag{1.1}$$

where the states with n = 0 (hole) and n = 2 (pair in the s^2 configuration) are denoted by 0 and 2. Thus, for a system of s-electrons (if we confine our attention to only s-states and normalize the sum of their occupation numbers to unity) the action of a_σ^+ is equivalent to the action of the transition operators which transform the system from the state 0 into σ and from $-\sigma$ into 2.

One can easily verify that the coefficients in Eq. (1.1) (in the same way as in formula (1) in the general case) are chosen so as to guarantee all commutation relations and normalization conditions, provided the commutation rules for the X-operators proposed by Hubbard[4] are satisfied.

APPENDIX 2

The coefficients of thc Hamiltonian (3) have the form

$$\varepsilon_\nu(\Gamma_n)=\int |R_{\Gamma_n}(r)|^2\left\{\frac{p^2}{2m}+V_\nu(r)\right\}r^2dr, \tag{2.1}$$

$$Q_\nu^l(\Gamma_n)=\sum_{\Gamma_{n-1}\Gamma_{n-2}L'_{n-1}\varkappa}[l]^2\begin{pmatrix} l & \varkappa & l\\ 0 & 0 & 0\end{pmatrix}^2F_\nu^\varkappa(\Gamma_n)([L_{n-1}][L'_{n-1}])^{1/2}\cdot \tag{2.2}$$

$$\times G^{\Gamma_n}_{\Gamma_{n-1}}G^{\Gamma_n}_{S_{n-1}L'_{n-1}}G^{\Gamma_{n-1}}_{\Gamma_{n-2}}G^{S_{n-1}L_{n-1}}_{\Gamma_{n-2}}(-1)^{\varkappa+L_n+L_{n-2}}\begin{Bmatrix} L_{n-1} & L_n & l\\ l & \varkappa & L'_{n-1}\end{Bmatrix}\begin{Bmatrix} \varkappa & L'_{n-1} & L_{n-1}\\ L_{n-2} & l & l\end{Bmatrix},$$

$$F_\nu^\varkappa(\Gamma_n)=e^2\int |R_{\Gamma_n}(r_1)|^2|R_{\Gamma_n}(r_2)|^2\frac{r_<^\varkappa}{r_>^{\varkappa+1}}r_1^2r_2^2dr_1dr_2, \tag{2.3}$$

$$B(\nu_1\Gamma_{n_1},\nu_2\Gamma_{n_2-1};\nu_1\Gamma_{n_1-1},\nu_2\Gamma_{n_2})$$

$$=(n_1n_2)^{1/2}\sum_{\gamma_1\gamma_2}G^{\varphi_1}_{\Gamma_{n_1-1}}G^{\varphi_2}_{\Gamma_{n_2-1}}C^{\varphi_1}_{\gamma_1,\Gamma_{n_1-1}}C^{\varphi_2}_{\gamma_2,\Gamma_{n_2-1}}\beta(\nu_1\gamma_1,\nu_2\gamma_2),$$

$$\beta(\nu_1\gamma_1,\nu_2\gamma_2)=\int \psi^*_{\nu_1\gamma_1}(r)V(r)\psi_{\nu_2\gamma_2}(r)dr, \tag{2.4}$$

where $R_{\Gamma_n}(r)$ are the radial functions representing the solution of the Hartree-Fock equation for an atom with configuration l^n in the state Γ_n, $\varphi_1=\Gamma_{n_1}$, and $\varphi_2=\Gamma_{n_2}$. The quantities

$$\begin{pmatrix} l & \varkappa & l\\ 0 & 0 & 0\end{pmatrix},\ \begin{Bmatrix} \varkappa & L' & L\\ L_1 & l & l\end{Bmatrix}$$

are the 3j and 6j symbols, $\kappa=0\ldots 2l$.

We also present here certain useful relationships

$$\sum_\gamma a_\gamma^+a_\gamma=\sum_{n\Gamma_n}nX(\Gamma_n),\quad \sum_\gamma a_\gamma a_\gamma^+=\sum_{n\Gamma_n}(2[l]-n)X(\Gamma_n). \tag{2.5}$$

The addition formulas

$$n\sum_{\Gamma_{n-1}}G^{\Gamma_n}_{\Gamma_{n-1}}G^{\Gamma_n'}_{\Gamma_{n-1}}C^{\Gamma_n}_{\gamma',\Gamma_{n-1}}C^{\Gamma_n'}_{\gamma,\Gamma_{n-1}}+(n+1)\sum_{\Gamma_{n+1}}G^{\Gamma_{n+1}}_{\Gamma_n}G^{\Gamma_{n+1}}_{\Gamma_n'}C^{\Gamma_{n+1}}_{\gamma,\Gamma_n}C^{\Gamma_{n+1}}_{\gamma',\Gamma_n}$$
$$=\delta_{\Gamma_n\Gamma_n'}\delta_{\gamma\gamma'}, \tag{2.6}$$

$$([S_n][L_n])^{-1}\sum_{S_{n+1}L_{n+1}}(G^{S_{n+1}L_{n+1}}_{S_nL_n})^2[S_{n+1}][L_{n+1}]=\frac{2[l]-n}{n+1},$$
$$[a]\equiv 2a+1, \tag{2.7}$$

were used in the derivation of Eqs. (2) and (2.5); the validity of formulas (2.6) and (2.7) can be verified directly in each specific case.

APPENDIX 3

The average values (introduced in the main text of this article) of the functions of diagonal operators $\hat\Phi(X(\Gamma_n))$ can be calculated in the following manner. To begin with let us write down the normalized second-quantization functions for a system of $N\bar n$ electrons, forming i_1, $i_2\ldots$single-particle states, pairs, etc. Assuming that all of the second-quantized functions with given numbers i_1, $i_2\ldots$and differing distributions over the N sites are degenerate in the zero-order approximation for the Hubbard model, we may introduce the functions

$$c_N(i_1i_2\ldots)=[N!/i_1!i_2!\ldots(N-i_1-i_2-\ldots)!]^{1/2}c_{i_1i_2\ldots}(n_1n_2\ldots), \tag{3.1}$$

where the factorial multiplier takes the degeneracy of the given class of functions into account.

Then, in calculating the matrix elements of diagonal operators one can obviously use the functions $c_N(i_1i_2\ldots)$ instead of $c_{i_1i_2\ldots}(n_1n_2\ldots)$, by introducing the additional factor $i_1!i_2!\ldots(N-i_1-i_2-\ldots)!/N!$ into the result.

For example, let us evaluate the following matrix element:

$$\overline{\Phi_N(i_1i_2)}=\langle c_{i_1i_2}(n_1n_2\ldots)|\frac{1}{i_1!\,i_2!}\sum_{\{\nu_1\}\{\nu_2\}}\prod_{\nu_1}^{i_1}X_{\nu_1}(\Gamma_1)\prod_{\nu_2}^{i_2}X_{\nu_2}(\Gamma_2)|c_{i_1i_2}(n_1n_2\ldots)\rangle \tag{3.2}$$
$$=\frac{i_1!\,i_2!(N-i_1-i_2)!}{i_1!\,i_2!\,N!}\sum_{\{\nu_1\}\neq\{\nu_2\}}^{i_1}\sum^{i_2}1=\frac{(N-i_1-i_2)!}{N!}N(N-1)\ldots(N-i_1-i_2+1)=1,$$

i.e., we actually obtain the correct result.[8]

Upon decoupling the Green's functions with separation of one or two particles, the space of the wave functions c_N decomposes as follows:

$$c_N(i_1i_2\ldots)=c_{N-1}(i_1-1,\ i_2\ldots)c_1(1),$$
$$c_N(i_1i_2\ldots)=c_{N-2}(i_1-1,\ i_2-1\ldots)c_2(1,2), \tag{3.3}$$

and the appropriate factorial multiplier for the function

$c_{N-1}(i_1-1,\ldots)$ is $[(i_1-1)!i_2!\ldots(N-i_1-i_2-\ldots)!]/(N-1)!$

Taking this into account, we have the following expression for the operator $\hat\Phi$ in the term corresponding to pair transfer in Eq. (13):

$$\overline{\Phi_{N-1}(i_2-1,i_3)}=\frac{(N-i_2-i_3)!}{(N-1)!}$$
$$\times\sum_{\nu_2\neq\ldots\neq\nu_{i_2+i_3}(\neq\nu_1,\nu_1')}\langle c_{N-1}(i_2-1,i_3)|\prod_{\nu_2}^{i_2-1}X_{\nu_2}(\Gamma_2)\prod_{\nu_3}^{i_3}X_{\nu_3}(\Gamma_3)|c_{N-1}(i_2-1,i_3)\rangle \tag{3.4}$$
$$=\frac{(N-i_2-i_3)!}{(N-1)!}(N-2)\ldots(N-i_2-i_3)=\frac{N-i_2-i_3}{N-1}=\frac{i_1}{N-1}\approx\bar i_1=\overline{X(d)}.$$

Similarly for the transfer of a triplet, and for the annihilation and creation of pairs we obtain

$$\overline{\Phi_{N-2}(i_2-1,i_3-1)}=\frac{(N-i_2-i_3)!}{(N-2)!}.$$
$$\times\sum_{\nu_2\neq\ldots\neq\nu_{i_2+i_3-1}(\neq\nu_1,\nu_1')}\langle c_{N-2}(i_2-1,i_3-1)|\prod_{\nu_3}^{i_3-1}X_{\nu_2}(\Gamma_2) \tag{3.5}$$
$$\times\prod_{\nu_3}^{i_3-1}X_{\nu_3}(\Gamma_3)|c_{N-2}(i_2-1,i_3-1)\rangle=1;$$
$$\overline{\Phi_{N-2}(i_2-2,i_3)}=1;\quad \overline{\Phi_{N-1}(i_2,i_3-1)}=\overline{X(d)}.$$

These results have a simple physical meaning. The probability for the transfer of a pair to singly occupied sites is proportional to the number of such sites; the same is true with regard to the probability for the annihilation of a triplet (i.e., the creation of a pair). In the probability for the transfer of a triplet to doubly occupied sites and the creation of a triplet, the quantities $\overline{\Phi}$ give a factor equal to unity, that is, these processes do not vary. Such an asymmetry is associated with the choice of the ground state. In our case only two (pairs and triplets) of the three types of states are assumed to be independent quasiparticles, and the third (single-particle) is selected as the ground state. This is the reason why only $X(\Gamma_2)$ and $X(\Gamma_3)$ operators appear in $\hat{\Phi}$ while the operators $X(\Gamma_1)$ are absent. The terms $X_{\nu_1}(\Gamma_3\Gamma_2)X_{\nu_1'}(\Gamma_2\Gamma_3)$ which transfer a triplet can simultaneously be considered as pair-transfer terms. The probability (associated with the factor $\overline{\Phi}$) for such processes is close to unity even for complete occupation of N-1 sites by pairs (the triplet is moving over doubly occupied sites) and also by triplets (the pair is moving over triply occupied sites). Such a situation would also occur for the transfer of pairs $X_{\nu_1}(\Gamma_2\Gamma_1)X'_{\nu_1}(\Gamma_1\Gamma_2)$ if the $X_\nu(\Gamma_1)$ were independent quasiparticles and if they appeared in $\hat{\Phi}$.

For a different choice of the ground state one can obtain $\overline{\Phi_{N-2}(i_2-1, i_3-1)} \approx \overline{\Phi_{N-2}(i_2-2, i_3)} \approx i_2$; however, in our case this does not change the results since we are considering $\overline{i}_2 \approx 1$ and $\overline{i}_3 \approx \overline{i}_1 \ll 1$.

The whole picture is to some extent analogous to Einstein transitions between levels where, as is well known, the probabilities for such transitions depend on the populations of the levels.

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[1] In actual fact Eqs. (15) constitute only a block-scheme without taking the spin and orbital projections into account; however, this will be adequate for our considerations.

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