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The tight-binding approach to the corundum-structure d compounds

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Abstract. The analysis of electronic structures has been carried out for the transition-metal compounds showing the corundum-type crystal symmetry using the suggested tight-binding method for interacting bands. With the self-consistent field approximation, the branches of the electronic spectra and energy gaps have been analytically calculated. The role of the electron correlations was found to be decisive for the dielectrization of spectra for which no additional assumptions, e.g. the existence of spin- or charge-density waves, was necessary. The data obtained provide an explanation for the appearance of the insulator state in such compounds as Ti_2O_3, V_2O_3, Cr_2O_3, α-Mn_2O_3 and α-Fe_2O_3. The calculated values of band gaps agree reasonably with the experimental data available. The Peierls problem is solved for the corundum-structure d compounds.

1. Introduction

The nature of the insulator state in the ionic compounds of non-metals with transition metals (TMs) with incomplete shells is thought to be among the central problems of modern solid state physics. In spite of the presence of unoccupied bands, most of these compounds are insulators, contrary to the predictions of the conventional one-electron band theory (compare, e.g., [1]). Extending the Hubbard [2] model to the orbital degeneracy of electrons and using the sequential diagram technique to account for intra-atomic correlations, the method of strong coupling for interacting bands has been proposed [3] (see sections 2 and 3). This method generalizes the traditional Slater–Koster approach for non-interacting electrons. The proposed tight-binding method for correlated electrons suggests that insulating gaps at homogeneous paramagnetic phases of TM compounds may result from the intra-atomic interactions of electrons, a problem formulated by Peierls in 1937. The Mott–Hubbard d compounds of rock-salt structure (space group, $O_h^5(Fm3m)$) act as insulators with half-filled e_g and t_{2g} bands. The same is true for spinel-type compounds of the magnetite (Fe_3O_4) type in the mixed-valence state [4]. In the opposite case of the non-half occupation of classical Slater–Koster bands, the metallic state is observed (e.g. ScO and TiO).

Another class of TM compounds, sesquioxides, which have a structure of the corundum (α-Al_2O_3) type of symmetry ($D_{3d}^6(R3c)$) is of practical importance. Most of them, e.g. Ti_2O_3 ($3d^1$), V_2O_3 ($3d^2$), Cr_2O_3 ($3d^3$), α-Mn_2O_3 ($3d^4$), α-Fe_2O_3 ($3d^5$) and Rh_2O_3 ($4d^6$) are insulators. At $T > T_N$ they are known to be present in the dielectric state of the non-magnetic phase up to the insulator–metal transition reported [5] for Ti_2O_3 and V_2O_3. In comparison with the cubic crystals, analysis of the insulator situation in the d compounds

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of the corundum type seems to be more intricate in view of the fact that the Bravais cell of α-Al_2O_3 has four cations and not one as in the case of the NaCl structure. Besides the Sommerfeld–Bethe [6] splitting found for the strongly correlated d electrons [3, 4], this results in an increased number of electronic bands due to the Davydov [7] splitting (cf section 3). The calculations of energy bands reported for Ti_2O_3 [8–10] and V_2O_3 [9–12] are, one way or another, on the level of the Hartree–Fock one-electron approximation with some additional assumptions and parameters to provide the formation of band gaps, bonding and antibonding orbitals, arbitrary band shifting and even their inversion [8, 11], electron-hole coupling in the presence of 'nesting' [9, 11], and distortions of the corundum cell [10, 11]. Computations of the low-temperature properties of V_2O_3 using the Hartree–Fock method with non-sphericity of the muffin-tin potentials, covalent bonding with anions, and orbital ordering of the 'antiferromagnetic' type taken into account, have been performed in a number of studies [12]. The one-electron calculations by the method of intersecting bands [13] demand an unwarranted number of fitting parameters. Indeed, modes of the exciton type, of charge- and spin-density waves, or types of orbital ordering may result in the formation of energy gaps in the electronic spectrum. In the best case this approximation may be used to predict the occurrence of antiferromagnetically and/or orbit-ordered phases of sesquioxides. However, for the homogeneous paramagnetic phases above the temperatures of ordering, such approximations give no insight into the nature of the dielectric state. The effort involved in calculating the electronic structure of TM compounds of corundum type grow in proportion with the number of electrons in the non-filled d shells of the cations, with no essential advance in the understanding of the nature of the dielectric state. Calculation of the band structures of Cr_2O_3, α-Fe_2O_3 and other oxides where the number of electrons exceeds two per cation are still lacking in the literature. On the contrary, the electronic systems under consideration are essentially correlated, and the positions of energy bands have been qualitatively analysed by Goodenough [14] and by Brinkmann and Rice [15] and have been discussed in the monograph by Mott [16].

A small change in temperature ($T > T_N$), which results in the breakdown of the AFM long-range ordering in the compounds of interest, mostly does not lead to disappearance of the band gap. Ordering vanishes, but the insulator gap remains. This energy gap may be eliminated in Ti_2O_3 and V_2O_3 by the action of pressure. Conservation of the insulator gap in the homogeneous spin- and orbit-disordered state of matter may be caused by strong intra-atomic Coulomb interactions of electrons; this problem has been formulated by Peierls in 1937 for a number of TM compounds (e.g. [1, 16]).

In the present work, it is shown how the electronic structure of TM sesquioxides may be obtained within the framework of models for strongly correlated electrons [2, 17]. The band gap at the Fermi level is formed owing not only to the interaction of electrons of one orbital (Ti_2O_3 and α-Mn_2O_3), but also to the interorbital interactions (in V_2O_3, Cr_2O_3 and α-Fe_2O_3). Using the proposed tight-binding method for interacting electrons, the electronic structures of Ti_2O_3, V_2O_3, Cr_2O_3, α-Mn_2O_3 and α-Fe_2O_3 are calculated analytically for the orbitally disordered paramagnetic insulator phase. The alternative mechanisms [4, 18] of the insulator–metal transition discovered [5, 16] for Ti_2O_3 and V_2O_3 are not discussed here.

2. Formulation of the problem

The strong octahedral crystal field in the corundum lattice removes the fivefold degeneracy of the 3d orbitals of electrons localized at cations, which are two thirds of the total number of octahedral vacancies. The trigonal component D_{3d}^6 of the crystal field reduces in turn

the threefold degeneration of the split t_{2g} orbitals to doublets and singlets. Within the $\{x', y', z'\}$ reference system of the 'oxygen' sublattice of corundum, the basic functions for the one-dimensional $a_{1g}(c)$ and two-dimensional $e_g(\pi)(a, b)$ irreducible representations may be written as follows:

$$\psi_c = \left(1/\sqrt{3}\right) f(r)(y'z' + z'x' + x'y')$$

$$\psi_a = \sqrt{\tfrac{2}{3}} f(r)[x'z' + \tfrac{1}{2}(x' + z')y'] \qquad \psi_b = \left[f(r)/\sqrt{2}\right](x' - z')y' \tag{1}$$

where

$$f(r) = \sqrt{15/\pi} \exp(-r^2/r_B^2)/2r^2.$$

Writing the ψ-values in the invariant vector form and changing to the reference system $\{x, y, z\}$ related (figure 1) to the sublattice of metal ions, we obtain the basic functions

$$a_{1g} : \psi_c = \left[f(r)/2\sqrt{3}\right](2z^2 - x^2 - y^2)$$

$$e_g(\pi) : \psi_a = \sqrt{\tfrac{1}{3}} f(r)\left[(y^2 - x^2)/\sqrt{2} - yz\right] \qquad \psi_b = \left[f(r)/\sqrt{3}\right] x \left(y\sqrt{2} + z\right). \tag{2}$$

The same result may be obtained conventionally (compare, e.g., [12]) where the invariant vector form of the elementary cell of corundum is now represented as a skewed hexagonal prism (figure 1) instead of the well known [19] hexagonal configuration. In figure 1, two of its six layers are shown. Each metal ion is surrounded by six oxygen ions (not shown in figure 1) thus inducing the octahedral crystal field. Along the z axis, the O-4 pairs of cations are alternating. Using the translation vectors τ_1, τ_2 and τ_3, all 28 cations of the corundum elementary cell may be obtained from two positions 0 and 1, and not from four, as is widely accepted [19].

Of the TM sesquioxides, V_2O_3 shows the largest and Ti_2O_3 the smallest c/a-ratio, while Cr_2O_3 and α-Fe_2O_3 have intermediate c/a-ratios [12]. For this reason, using the notation of (2) and following the qualitative considerations of Goodenough [14], the ground state of the 3d ions in the compounds under consideration may be represented as Ti_2O_3 (a_{1g}^1), V_2O_3 ($e_g^2(\pi)$) and Cr_2O_3 ($a_{1g}^1 e_g^2(\pi)$). According to one classification [20–22], both holes and electrons in these oxides are heavy and move in d bands. The nature of the insulator gap in these compounds is of the Mott–Hubbard (d–d) type rather than the charge-transfer (2p–3d) type. These conclusions are borne out by estimates in [23–25].

Therefore it is primarily essential to take into consideration the effects of intra-atomic d–d correlations: one-orbital-type interactions I (Hubbard), interorbital-type interactions U (Coulomb) and J (Hund). The effects of covalency and ionic polarizability or the motion of the atoms in the ionic M_2O_3 crystals under consideration are not included in this approach. With multi-electronic terms of the ground state, the one-call Hamiltonian (for 0 and 1 atoms from the elementary cell unit in figure 1) may be diagonalized:

$$H_1 = \sum_{r,k} \varepsilon_k X_r^{kk}. \tag{3}$$

Here ε_k are the energy levels of the m lowest Bose states (with an even number of electrons) and of the n lowest Fermi states (with an odd number of electrons), and X^{kp} are the X-operators projecting a cell from the p to k energy state. The essential intra-atomic
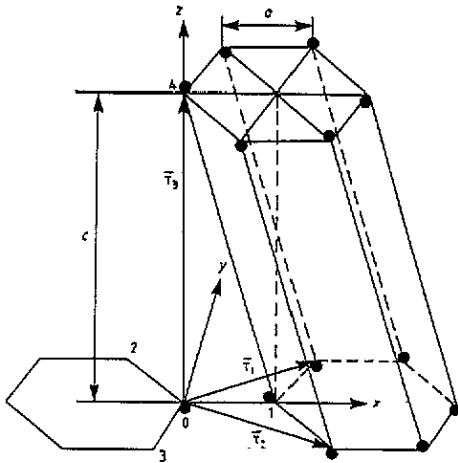
Figure 1. Two cation layers from six layers of the elementary cell of corundum structure. The vectors of lattice translations are $\tau_1 = \{\frac{3}{2}, \sqrt{3}/2, 0\}a$, $\tau_2 = \{\frac{3}{2}, -\sqrt{3}/2, 0\}a$ and $\tau_3 = \{a, 0, c\}$.
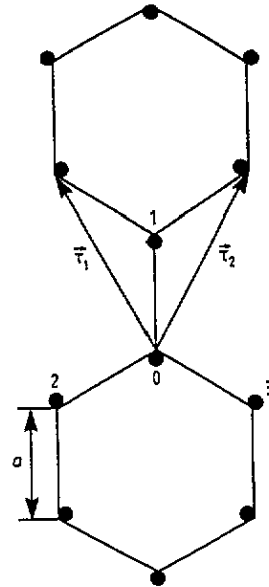
Figure 2. The cation packing in the basal plane.

electronic interactions (Hubbard, Coulomb and Hund) enter the problem at the energy levels ε_k. Application of the Hund rule and the Pauling principle of electric neutrality makes it possible [3] to consider elementary excitations within the convenient basis of the spl(m, n) superalgebra, thus avoiding application of the superalgebras of higher ranks. Expansion of the one-electron operators of creation and annihilation over the Hubbard X-operators is determined by the genealogical coefficients g_α:

$$a_\sigma = \sum_\alpha g_\alpha X^{\alpha(k,p)}. \tag{4}$$

Further we confine ourselves to the translations between the degenerate ground and polar states. For the half-filled bands the chemical potential has to be chosen so that the polar states would have the same energy.

The tunnel part of the Hamiltonian is represented via all possible products of the X-operators for neighbouring cells:

$$H_2 = \sum_{\alpha,\beta,r,r'} t_{\alpha\beta}(r - r')X_r^\alpha X_{r'}^\beta. \tag{5}$$

The $t_{\alpha\beta}(r)$-matrix is determined by the matrix of effective interaction hopping integrals:

$$t_{\alpha\beta}^{ab}(p) = g_\alpha^a t^{ab}(p)g_\beta^b \tag{6}$$

where $t^{ab}(p) = \sum_r t^{ab}(r)\exp(ipr)$, $t^{ab}(r)$ is the effective interaction hopping integral of electrons from orbital b to orbital a at distance r via the intermediate oxygen anions:

$$t_{ij}^{ab} = \int \psi_{ia}^*(r)V(r)\psi_{jb}(r - a)\,\mathrm{d}r. \tag{7}$$

3. The tight-binding method for interacting bands: general consideration of the electronic spectra

The diagram method for X-operators is based on the generalized Wick theorem [26], which has been repeatedly proved for spl(2, 2) superalgebra of X-operators in the Hubbard model [27–29]. The diagram technique for Hubbard operators has been worked out analogously to that for Heisenberg operators [30] and can therefore be easily adapted to superalgebras of higher rank [3, 31].

The desired spectrum of the one-particle excitations is determined by the poles of the appropriate Green function

$$D_{\alpha\beta}(rt, r't') = -\langle \hat{T} X_r^{\alpha}(t) X_r^{-\beta}(t') \rangle. \tag{8}$$

The initial (zeroth) Green function has the form

$$D_{\alpha(k,p)}^{(0)}(\omega_n) = (n_p + n_k)(-i\omega_n + \varepsilon_p - \varepsilon_k)^{-1} \tag{9}$$

where n_p and n_k are the Boltzmann populations of the p and k energy levels, and $\alpha(k, p)$ (root of spl(m, n)) denotes the atomic transition between them, accompanied by a change in the number of electrons by unity. The small parameters of the diagram technique consists of

    (1) the inverse number of nearest neighbours,
    (2) the particle concentration near correlation band edges (gaseous approximation), and
    (3) the hopping integrals (equation (7)) rendered dimensionless by intra-atomic correlations I, U and J.

In higher orders of perturbation theory the scattering of excitations at the spin, charge and orbital fluctuations results in the disappearance of the correlation gap and in the occurrence of the Mott–Hubbard phase transition. Here these effects are not taken into account because traditional Slater–Koster [32] equations (LCAO method) describe bands of non-interacting electrons in the first order of hopping integrals. The sequential diagram technique for generalized X-operators may be followed to yield the different ordered states of realistic models similar to [4, 33, 34].

When the necessary transformations $i\omega_n \rightarrow E + i\delta$ have been performed in equations (8) and (9), the Dyson equation for inverse Green function (8) within the first-order perturbation theory leads to the following secular equation:

$$\det \|[D_{\alpha}^{(0)}(E)]^{-1}\delta_{\alpha\beta} + t_{\alpha\beta}(p)\| = 0.$$

This equation determines the single-particle energies forming correlated energy bands. The determinant consists of $l \times l$ blocks numbered by degenerate orbitals $l = m + n$, the size of each square block equalling the number of components in the decomposition (4). By decomposing this determinant along diagonal elements, which are linear relative to energies E, according to the procedure in [3], we obtain the following system:

$$\sum_{\alpha} g_{\alpha}^2 D_{\alpha}^{(0)}(E) = -\varepsilon^{-1}(p) \tag{10}$$

$$\det \|t_{mn}(p) - \varepsilon\delta_{mn}\| = 0. \tag{11}$$

Here the effective transfer integral $\varepsilon(p)$ is the solution of the l-dimensional (l is the orbit degeneration factor) secular equation (11) to which in its turn the Schrödinger equation in the Slater–Koster [32] approach may be reduced for non-correlated electrons. The off-diagonal elements (7) in the matrix (11) determine the well known splittings for non-interacting electrons governed either by the number of orbitals in an atom (the Sommerfeld–Bethe splitting) or by the number of atoms in a cell (the Davydov splitting). The matrix elements in (11) have been calculated previously; they are known as the so-called integrals of Slater and Koster. In the first equation of the system (10)–(11), the effects of the intra-atomic electronic interactions I (Hubbard), U (Coulomb) and J (Hund) are manifested in the correlation splitting of every Sommerfeld–Bethe or Davydov subband of the Slater–Koster method into the correlated bands. For the conventional orbitally non-degenerate Hubbard [2] model, equation (10) can be reduced to the simple equation

$$(n_0 + n_+)/(-E + \varepsilon_{+0}) + (n_- + n_2)/(-E + \varepsilon_{-2}) = -1/\varepsilon(p)$$

where $\varepsilon(p)$ is the dispersion law for non-interacting s electrons [2].

Within the framework of the considered model (3)+(5) of the real crystal with orbital degeneracy, the branches of the electronic spectrum $E(p)$ derived from (10) and (11) determine the band gap

$$\Delta_g = E^{LUB}(\varepsilon_{min}^{LUB}(p)) - E^{HOB}(\varepsilon_{max}^{HOB}(p)) \tag{12}$$

where E^{LUB} and E^{HOB} are the lowest unoccupied band and highest occupied band energies of correlated electrons.

The TM compounds under consideration represent ionic crystals in which the wavefunctions of the cation are localized on a scale of the magnitude of r_B (the Bohr radius or ionic radius), which is small compared with the lattice parameter a. For this reason in the determinant equation (11) the remaining transfer integrals are of the same small magnitude as the parameter r_B/a. This parameter ensures narrow energy bands, high intra-atomic energies I, U and J and an ionic character of solids under consideration. The small parameter r_B/a gives us the opportunity to evaluate the hopping integrals as proposed in [3], suitable for our strong-coupling-like approach. The product of radial parts $f(r)$ of the wavefunctions is maximal at half the interion distance, which makes a perfect origin of coordinates for use in equation (7). The radial parts $f(r)$ decrease exponentially with increasing distance and can be approximated by Gaussians as $f(r) \sim \exp(-r^2/r_B^2)$. We can therefore arrive at the hopping integral (7) of any required accuracy in the form of the power series of $(r_B/a)^2$. For the main crystal Bravais lattices we can probably calculate all matrix elements for the tight-binding method in [35] for hydrogen-like parts of d wavefunctions, if in equation (7) we restrict ourselves to terms of the order $(r_B/a)^3$. Non-spherical wavefunctions of electrons ensure anisotropy in layer-structured high-T_c cuprates [36].

In the present work, the off-diagonal transfer integrals (7) for the $e_g(\pi)$ and a_{1g} orbitals along the c axis are of the order $(r_B/a)^5$ and may therefore be neglected. It is essential that the overall non-diagonal elements (with transfer within the basal plane taken into account) for the $e_g(\pi)$ and a_{1g} orbitals are of the order $(r_B/a)^3$, i.e. comparable with the diagonal elements. Within the basal plane of the corundum structure, the cations are packed into the two-dimensional lattice of the honeycomb structure, as shown in figure 2. In calculating the hopping integrals (7), we confined ourselves to tunnelling only to the nearest neighbours 1, 2, 3 and 4 from the centre 0 (see figures 1 and 2), owing to the exponential decrease in the radial wavefunctions (1).

4. Electronic structure of the a_{1g}^1 compounds of transition metals (Ti_2O_3)

The electronic ground state of cations with a half-filled a_{1g} shell is the singlet state. The a_{1g} electrons are described by the wavefunction $\psi_c(r)$ (equation (2)). The expansion (4) of the one-electron operators over atomic X-operators is coincident with the expansion for the non-degenerate Hubbard [2] model [3]. Dividing the two-dimensional honeycomb lattice in figure 2 into two sublattices of the 0 and 1 type, we find that equation (11) acquires the simple form of a 2×2 determinant with enumeration of rows 0 and 1 (cf figures 1 and 2):

$$\begin{matrix}(0)\\(1)\end{matrix}\begin{vmatrix} \varepsilon & t(p) \\ t^*(p) & \varepsilon \end{vmatrix} = 0. \tag{13}$$

Here

$$t(p) = \tfrac{2}{3}t[1 + 2\exp(-iX)c_Y + t^c\exp(iZ)]$$

are the elements of the transfer matrix in (11) and $X = \tfrac{3}{2}ap_x$, $Y = a\sqrt{3}p_y/2$, $Z = -ap_x + cp_z = -\tfrac{2}{3}X + cp_z$ and $c_\alpha = \cos\alpha$. In further discussion, all the electron branches will contain the invariants with respect to rotation at the $\tfrac{2}{3}\pi$ combination of the trigonometric functions:

$$\eta = 2c_Y c_{(X+Y)/2} c_{(X-Y)/2} \qquad \zeta = c_Z + c_{X-Y+Z} + c_{X+Y+Z}. \tag{14}$$

Substituting the effective transfer integral from (13) into (10) the following four branches of the electronic spectrum are obtained:

$$E_{1,2}(p) = \tfrac{1}{2}(|t(p)| \pm \sqrt{|t(p)|^2 + 4\Delta^2}) = -E_{4,3}(p) \tag{15}$$

where $\Delta = I/2$ is half the Hubbard energy of electrons from the non-degenerate orbital a_{1g}. The absolute value of the transfer integral in solution (15) is given via the invariants (14) and the amplitudes of the transfer integrals t and t^c within the basal plane and along the c axis respectively:

$$|t(p)| = \tfrac{2}{3}t\sqrt{1 + 4\eta + 3t^c\zeta/t + (3t^c/2t)^2} = \varepsilon_{1,2}(p). \tag{16}$$

Dimerization of the titanium ions along the c axis of the hexagonal elementary cell leads to the Davydov dimeric splitting of energy bands:

$$D = \min[E_2(p) - E_4(p)] = \min|t(p)| = t^c - 2t(t^c > 2t)$$

at the $Z(0, 0, \pi/c)$ point of the Brillouin zone. For Ti_2O_3, let the typical hopping integrals have the following values [9]: $t^c = 0.9$ eV; $t = 0.15$ eV. Then the dimeric gap is $D = 0.6$ eV and is independent of the correlation energy $\Delta = I/2$. The role of the correlation gap is reduced here to splitting the empty branches of the electronic spectra $E_1(p)$ and $E_3(p)$. Therefore, when $t^c > 2t$, separation of the bonding and antibonding orbitals (the Davydov splitting of the non-interacting electrons) may cause the dielectric state of the non-correlated spectrum (16) to occur. The bonding and antibonding orbitals have already been used [13, 37] to take into account qualitatively the insulator properties of Ti_2O_3. Under conditions of strong correlation ($\Delta \neq 0$), two electrons of cations 0 and 1 (see figure 2) occupy the two isolated branches of the electronic spectrum, $E_2(p)$ and $E_4(p)$ (equation (15)). Other branches are empty and separated by a band gap of correlation type.

It should be noted that in Ti_2O_3 the observed [8] activation energy $E_g = 0.02$–0.06 eV is smaller than the dielectric gap derived from solutions (15). For crystals of high purity, this is probably because, for Ti_2O_3 above $E_F = 0$, in the vicinity of the calculated band energies $E_2(p)$ and $E_4(p)$ there exist unoccupied levels of the e_g doublet that are separated by a weak crystal-field distance of 200 cm, which is close to E_g in magnitude.

5. Electronic structure of the $e_g^2(\pi)$ compounds of V_2O_3 type

According to [14, 15], we shall assume that in vanadium sesquioxide the $e_g^2(\pi)$ doublet is lower than the a_{1g} singlet by a value exceeding the tunnelling energy. In such a case the ground state of the V^{3+} cation with the half-filled $e_g(\pi)$ shell is an orbital triplet. Expansion (4) of the Fermi operators, from which the ground-state electronic term of vanadium is formed, is similar to expansion of the a- and b-operators in the double-degenerate Hubbard model in [31]. Consideration is given to the basis of superalgebra spl(3, 8) [3]. So, equation (11) is reduced to the form

$$
\begin{matrix}
0 \begin{cases} a \\ b \end{cases} \\
1 \begin{cases} a \\ b \end{cases}
\end{matrix}
\begin{vmatrix}
\varepsilon & 0 & t^a(p) & t^{ab}(p) \\
0 & \varepsilon & t^{ba}(p) & t^b(p) \\
(t^a(p))^* & (t^{ba}(p))^* & \varepsilon & 0 \\
(t^{ab}(p))^* & (t^b(p))^* & 0 & \varepsilon
\end{vmatrix} = 0.
$$

The matrix elements have the following form of the transfer integrals:

$$t^a(p) = \tfrac{2}{3}t[2 + \exp(-iX)c_Y] \qquad t^b(p) = 2t\exp(-iX)c_Y$$

$$t^{ab}(p) = -\tfrac{2}{3}2it\exp(-iX)s_Y$$

where $s_Y = \sin Y$. From the last determinant equation the effective transfer integral is found that displays four branches:

$$\varepsilon_{1,2}(p) = -\tfrac{4}{3}t\sqrt{\tfrac{5}{2} + \eta\sqrt{(\tfrac{5}{2}+\eta)^2 - 9(1+4\eta)}} = -\varepsilon_{4,3}(p). \tag{17}$$

Spectrum (17) for non-interacting electrons with several hopping integrals was calculated [9] using the Slater–Koster method. By substituting (17) into (10), we obtain the four lowest bands, which will be occupied by four electrons of the 0–1 pair of vanadium cations V^{3+} (see figure 2):

$$E_k(p) = -\tfrac{1}{2}\varepsilon_k(p) - \sqrt{[\tfrac{1}{2}\varepsilon_k(p)]^2 + \Delta^2} \qquad (k = 1, 2, 3, 4). \tag{18}$$

According to (12), the correlation gap is determined by the maximal value of the highest occupied branch $E_4(p)$:

$$\Delta_g = -\max[\varepsilon_4(p)] + \sqrt{\{\max[\varepsilon_4(p)]\}^2 + 4\Delta^2} = 2\left(\sqrt{9t^2 + \Delta^2} - 3t\right). \tag{19}$$

In (18) and (19), $\Delta = \tfrac{1}{2}(U + J)$, where U and J are the Coulomb and Hund integrals, respectively. Taking the typical values of $U = 1.3$ eV, $J = 0.1$ eV and $t = 0.8$ eV [10], the energy gap $\Delta_g = 0.2$ eV is obtained from (19), which is in agreement with the experimental data available [16] for V_2O_3.

It should be emphasized that the results (18) and (19) obtained concern the completely disordered homogeneous paramagnetic phase, in which the band gap is determined exclusively by the intra-atomic interorbital interactions of electrons U and J.

Contrary to Ti_2O_3, the electronic spectrum (17) of the non-interacting electrons turns out to be gapless and degenerate at the points $Q(4\pi/9a, 4\pi\sqrt{3}/9a)$, $\Gamma(0, 0)$:

$$E_1(Q) = E_4(Q) = 0 \qquad E_2(\Gamma) = E_1(\Gamma) = -E_3(\Gamma) = -E_4(\Gamma) = -6t.$$

In view of $e_g(\pi)$-electron tunnelling within the basal plane, the separate consideration of only the bonding and the antibonding orbitals in the absence of interelectronic interaction could not provide an adequate description of the dielectric state.

6. Electronic structure of the $e_g^2(\pi)a_{1g}^1$ transition-metal compounds (Cr_2O_3)

The parameter c/a for the crystal Cr_2O_3 of corundum type has some intermediate value [12] between those for Ti_2O_3 and V_2O_3. For this reason, the electronic ground state of the Cr^{3+} cation is the quartet state. The intra-atomic situation is the same as for t_{2g} cubic crystals. Electronic excitations are considered in the basis spl(18, 4). Let the basis functions (2) describe the $a_{1g}^1(c)$ and $e_g^2(\pi)(a, b)$ electrons. Then equation (11) for the effective transfer integral is the following (i.e. for the spectrum of independent electrons $\varepsilon(p)$):

$$
\begin{array}{c}
0 \left\{ \begin{array}{c} a \\ b \\ c \end{array} \right. \\
1 \left\{ \begin{array}{c} a \\ b \\ c \end{array} \right.
\end{array}
\begin{vmatrix}
\varepsilon & 0 & 0 & t^a(p) & t^{ab}(p) & t^{ac}(p) \\
0 & \varepsilon & 0 & t^{ba}(p) & t^b(p) & t^{bc}(p) \\
0 & 0 & \varepsilon & t^{ca}(p) & t^{cb}(p) & t^c(p) \\
(t^a(p))^* & (t^{ba}(p))^* & (t^{ca}(p))^* & \varepsilon & 0 & 0 \\
(t^{ab}(p))^* & (t^b(p))^* & (t^{cb}(p))^* & 0 & \varepsilon & 0 \\
(t^{ac}(p))^* & (t^{bc}(p))^* & (t^c(p))^* & 0 & 0 & \varepsilon
\end{vmatrix} = 0
$$

where $t^a(p)$, $t^b(p)$ and $t^{ab}(p)$ are defined in section 5, $t^c(p)$ in section 4, and

$$
t^{ac}(p) = \tfrac{2}{3}\sqrt{2}t[1 - \exp(-iX)c_Y] \qquad t^{bc}(p) = \frac{i2t}{3}\sqrt{2}\exp(-iX)s_Y.
$$

For the non-interacting non-correlated electrons, we obtain the six-band spectrum with two non-dispersing bands $\varepsilon_{3,4}$:

$$
\varepsilon_{1,2}(p) = \mp t\sqrt{4 + (t^c/3t)[3t^c/2t + 2\zeta + \sqrt{16(2 - \eta) + (3t^c/2t + 2\zeta)^2}]}
$$

$$
\varepsilon_{3,4} = \mp 2t \tag{20}
$$

$$
\varepsilon_{5,6}(p) = \mp t\sqrt{4 + (t^c/3t)[3t^c/2t + 2\zeta - \sqrt{16(2 - \eta) + (3t^c/2t + 2\zeta)^2}]}.
$$

Substituting these branches into equation (10), the desired occupied bands of the correlated electrons are found:

$$
E_k(p) = -\tfrac{1}{2}\varepsilon_k(p) - \sqrt{[\tfrac{1}{2}\varepsilon_k(p)]^2 + \Delta^2} \qquad (k = 1, 2, 3, 4, 5, 6). \tag{21}
$$

Note that there are two dispersionless bands among these six bands which are centred at ε_3 and ε_4. Only the interacting bands are given in (21), which are situated below $E_F = 0$. According to (12), the band gap is given by

$$
\Delta_g = -\max[\varepsilon_2(p)] + \sqrt{\{\max[\varepsilon_2(p)]\}^2 + 4\Delta^2} = \sqrt{(2t + t^c)^2 + 4\Delta^2} - 2t - t^c. \tag{22}
$$

Assuming that $\Delta = 2$ eV and $t = 0.8$ eV [11] and taking $t^c = 1.4$ eV [10], for the energy band we obtain $\Delta_g = 2$ eV which is in agreement with the reported [38] experimental value for Cr_2O_3.

The electronic spectrum for the non-interacting electrons (20) has some particular features due to the presence of the Davydov splitting. At $t^c = 0$, the spectrum (20) is triply degenerate; the bands $\varepsilon_{1,3,5}$ and $\varepsilon_{2,4,6}$ are centred at $\varepsilon_3 = -2t$ and $\varepsilon_4 = 2t$, respectively. There is always twofold degeneration within the Brillouin zone at the line $k = 0 = k_y$. At the same line at $t^c < 4t$, there is a point of threefold degeneration $\{0, 0, (a/c)\cos^{-1}(-t^c/4t)\}$,

at which $\varepsilon_{1,2} = \varepsilon_{3,4}$. At $t^c > 4t$, the dimeric gap appears between the local and lower bands:

$$D_{1,2-3,4} = 2t\{[1 + (t^c/t)(t^c/4t - 1)]^{1/2} - 1\}. \qquad (23)$$

At $t^c < 6t$, the Fermi level for non-correlated electrons would be expected to occur in the middle of the dimeric gap:

$$D_{5-6} = 2t\sqrt{4 + \tfrac{1}{2}(t^c/t)^2 - 2t^c/3t - (t^c/3t)\sqrt{6t/t^c + 3t^c/8t - 1}}. \qquad (24)$$

According to (24), the dielectric phase Cr_2O_3 would seem to be expected within the system of non-interacting electrons. However, since the value of t^c was estimated [11] as equal to $6t$, the energy band (24) is much smaller than the observed [38] activation energy: $D_{5-6} \ll 2$ eV. On the other hand, for Cr_2O_3 it cannot be excluded that the band gap (24) for the non-interacting electrons disappears owing to degeneracy of the spectrum (20) at a point. This is why the only reason for the appearance of the dielectric paraphase in Cr_2O_3 may be to account for correlation of the 3d electrons in the Cr^{3+} cation according to (21) and (22), and the energy gap (23).

7. Conclusion

In the present study in the framework of the strong-coupling approach for correlated electrons, the predominating part played by the intra-atomic correlations in determining the physical properties of the TM metal–non-metal compounds has been demonstrated according to Peierls' idea [1, 16, 22].

The energies obtained for the one-particle excitations (17), (18) and (21), determining the energy bands for the TM compounds of the corundum structure, are independent of the amplitudes of the effective interaction hopping integrals along the c axis and within the a–b plane, as well as of the values of η and ζ (14). Using the notation in (12), it may be shown that, upon rotation at $\tfrac{2}{3}\pi$,

$$X + Y \rightarrow -(X' - Y') \qquad X - Y \rightarrow 2Y' \qquad Z \rightarrow \tfrac{1}{3}X' - Y' + ck_z.$$

In other words, the values of η and ζ are invariant with respect to rotations around the trigonal axis and, as could be expected, show D_{3d}^6 symmetry of the corundum crystal structure. Cubic crystals of the NaCl type with half-occupancy of the 3d bands are insulators because of splitting due to the crystal field. A similar statement holds true [4] for the spinel-type structure. The present data prove the validity of this statement for hexagonal crystals of the corundum type as well: Ti_2O_3 ($S = \tfrac{1}{2}$; $3d^1 \equiv a_{1g}^1$); V_2O_3 ($S = 1$; $3d^2 \equiv e_g^2(\pi)$), Cr_2O_3 ($S = \tfrac{3}{2}$; $3d^3 \equiv a_{1g}^1 e_g^2(\pi)$).

The position of the hole levels at the Mn^{3+} in α-Mn_2O_3 ($S = 1$) is coincident with the position of the electronic terms in V^{3+} (V_2O_3). For this reason, the conclusions in section 5 for V_2O_3 are valid in view of the electron–hole symmetry and the homogeneous paramagnetic phase α-Mn_2O_3 ($T_N = 80$ K).

The electronic spectrum of the high-spin haematite α-Fe_2O_3 ($S = -\tfrac{5}{2}$; $3d^5 \equiv e_g^2(\pi)e_g^2(\sigma)a_{1g}^1$) under the conditions of electron–electron correlations is determined by the half-occupied a_{1g}, $e_g(\pi)$ and $e_g(\sigma)$ bands. According to the present theory, haematite is also a dielectric. However, in view of the high Néel temperature $T_N = 963$ K, the analysis

of its paramagnetic phase ($T > T_N$) is merely of abstract academic interest. The electronic structure of the low-spin paramagnetic phase of haematite ($S = \frac{1}{2}$; $3d^5 \equiv e_g^4(\pi)a_{1g}^1$) is determined by the half-occupied a_{1g} band, as is the case for Ti_2O_3 (section 4).

The electronic structure of Rh_2O_3 in its Rh^{3+} low-spin state ($S = 0$; $4d^6 \equiv a_{1g}^2e_g^4(\pi)$) is formed by the completely filled a_{1g} and $e_g(\pi)$ bands. That is why the insulator state of Rh_2O_3 is evident and was not analysed by us.

An attempt to calculate the electronic spectrum of V_2O_3 in its paramagnetic phase was undertaken by Nebenzahl *et al* [11] within the framework of the $e_g^2(\pi)$ band model. They used the strong-coupling method for non-interacting electrons. Their results may be obtained by neglecting in the formulae in section 5 the interaction of electrons ($\Delta = 0$). In such a case, the band gap between the branches $\varepsilon_2(p)$ and $\varepsilon_3(p)$ is absent, and thus we obtain the metallic phase. To avoid metallization, Nebenzahl *et al* [11] admit the unjustified assumptions about the distortion of the lattice in figure 2. However, the lattice of this oxide is not actually distorted in the high-temperature paramagnetic phase.

It was shown that the primitive cell in the corundum structure may be chosen so that the minimal number of atoms within the elementary unit cell of the cations sublattice turned out to be equal to 2. All 28 cations of the elementary cell may be obtained from these two positions by translation. The presence of several atoms in a cell defines the appearance of the calculated dimeric gaps arising from the Davydov splitting. The correlation splitting of each of the orbit subbands occurs in such a way that the paramagnetic phases of all the sesquioxides of TMs with half-filled orbital subbands turn out to be insulating.

The data obtained may be applied to the analysis of the electronic structure of the hexagonal TM borides. In the framework of the suggested tight-binding approach for correlated electrons it is possible to describe insulators and metals on the basis of the mother substances $LaTiO_3$ ($3d^1$), $CaVO_3$ ($3d^1$), $YTiO_3$ ($3d^1$), $LaVO_3$ ($3d^2$), $SrCrO_3$ ($3d^2$) and $CaCrO_3$ ($3d^2$) with crystal structures of the cubic perovskite.

Acknowledgments

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