# Fundamental ideas on metal-dielectric transitions in 3d-metal compounds

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The fundamental mechanisms of a metal-dielectric transition are examined. The multiband theory of the metal-dielectric transition is reviewed, as based on realistic models of the band structure of a set of oxides and sulfides of the 3d-metals in which the transition is accompanied by structural and magnetic phase transitions. In the multiband case new phases arise that were absent in the simplest single-band theories, yet at the same time are known experimentally. The metal-dielectric transition is studied in the Shubin-Vonsovskiĭ model. It is shown that allowance for screening of the long-range Coulomb interaction leads to a first-order transition. We describe the concept of the metallic order parameter, which is proportional near the transition point to the density of states at the Fermi level. The theory enables one to explain qualitatively many experimental data, mainly thermodynamic, on the oxides of vanadium and titanium and the sulfides of 3d-metals having a metal-dielectric transition. The pathways are discussed of further development of the theory for fuller description of all physical properties of the materials being studied. Cases are analyzed in which localized magnetic moments exist and are manifested alongside the band states.

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## 1. INTRODUCTION

The study of metal-dielectric transitions has broken down the classification traditional in solid-state physics of materials into metals and dielectrics in terms of the type of electronic spectrum and the filling of the bands of collectivized electrons.[1][1)] Many examples appeared around the middle sixties that violate the described classification. The materials that underwent a metal-dielectric transition turned out to be anomalous. That is, they had the properties of metals under certain external conditions (temperature, pressure, etc.) and of dielectrics under others.[3,4] As a rule, the transition between these two states is accompanied by a sharp change in the electric conductivity (up to a factor of $10^{10}$ in the oxides of vanadium) and in other physical properties, and has the character of a first-order transition. The metal-dielectric transition (MDT) is also related to the metal-semiconductor and the semimetal-semiconductor transitions. Most generally one adopts the definition of a MDT as a transition with a change in the type of conduction.

What has given rise to the steadily growing interest (for already two decades) in the MDT problem? First, the unusual combination and interconnection of electric, magnetic, elastic, and optical properties compels one to employ a complex approach including both theoretical and various experimental methods, if even for a qualitative understanding of the MDT phenomenon in each concrete material. Seocnd, the set of exotic properties renders MDT studies practically important (see Ref. 5). Third, the transformation of a metal into a dielectric impedes the onset of superconductivity with decreasing temperature. Since the MDT is observed in "poor" metals, the hope exists that the study of MDT's will

favor the solution of the problem of high-temperature super-conductivity.[6,7]

Evidently, at ultrahigh pressures any substance becomes a metal, since the wave functions of the electrons on adjacent atoms will overlap sufficiently at small enough interatomic distances. Striking examples of MDT's under pressure are the metallic phases of typical dielectrics, such as xenon, sulfur, and NaCl obtained in the Institute of High-Pressure Physics of the Academy of Sciences of the USSR (see, e.g., the Materials of the 2nd All-Union Conference on MDT's[8]).

Another example of MDT's is the Anderson transition in disordered systems, involving localization of electrons at the mobility threshold.[9] One usually studies an MDT of this type experimentally in doped semiconductors as a concentration-dependent transition at a sufficiently low fixed temperature.[10,11]

A third example of a MDT is offered by studying a Peierls transition in quasi-one-dimensional systems,[12] involving formation of charge-density waves (CDW's) or spin-density waves (SDW's).

Finally, there is a large class of compounds (mainly oxides and sulfides of transition metals) where an MDT is induced by relatively small changes of temperature ($\sim 10^2$ K) and pressure ($\sim 10$–$100$ kbar). Here the MDT in these substances can be accompanied by structural and magnetic phase transitions. Among compounds of the 4f-metals the MDT is often a transition with change of valency, as has been discussed in the review of Ref. 13. Our topic of discussion is the narrow-band compounds of the 3d-metals.

As we see it, one can distinguish three stages in the history of the study of MDT's. The first was fundamentally characterized by the accumulation of experimental data, and ended in the middle sixties. At this time MDT's were discovered in the oxides of vanadium and titanium and the sulfides of nickel and a number of other compounds. In this period Mott expressed some important qualitative ideas on the nature of the metal-dielectric transition (see, e.g., Refs. 14–16). Around this time such mechanisms of MDT's were already known as the Peierls transition, Wigner crystallization, and MDT's caused by antiferromagnetic ordering.[17]

The second stage is characterized by the study of various mechanisms of MDT's. It developed in many ways under the influence of the ideas and methods of the theory of superconductivity, especially its field-theoretical formulation.[18,19] This includes the theory of an exciton dielectric[20,21] and the theory of the transition of a narrow-band metal with a special form of Fermi surface into the dielectric state.[22,23] At this same time Hubbard proposed a rather simple model describing an MDT, based on Coulomb correlations.[24,25] These studies formulated the conditions necessary for a metal to convert into a dielectric. However, the treatment was conducted within the framework of very simple models of the electronic spectrum whose applicability to compounds of the transition metals aroused serious doubts.

And finally, definite progress was attained in the past ten years in describing MDT's in concrete substances or classes of substances. These advances involve, on the one

hand, the extension of the ideas of the theory of an exciton dielectric to more realistic models of the electronic spectrum of concrete substances, often resting on numerical calculations of the band structure. On the other hand, they involve the further development of the treatment of the Hubbard model (including internodal Coulomb and electron-phonon interactions and impurities) by the methods of continual integration[26] and the diagram technique for the Hubbard operators.[27]

To describe these advances, along with the unsolved problems of the theory of MDT's, is the theme of this review.

A large number of original studies, conference materials,[3,4,8,14] and reviews[5,15,28–32] have been devoted to the problem of MDT's in compounds of the 3d-metals. However, most of the reviews were written long ago and are somewhat outdated, while a recent monograph[32] is restricted to a narrow class of materials—the monosulfides of the 3d-metals. At the same time, a number of interesting experimental data has recently appeared, and new compounds have been synthesized possessing MDT's. The analysis of these data on the basis of the existing theories is also an aim of this review.

The fundamental distinction of a metal from a dielectric involves the differing response to an external weak electromagnetic field. The multielectron criteria of whether a substance is a metal or a dielectric have been treated in Refs. 2, 33, and 34. At the same time, no unambiguous answer currently exists to the question of the order parameter in an MDT.

From the single-electron standpoint a dielectric differs from a metal by the gap in the spectrum. However, the gap is not a thermodynamic parameter and hence cannot be an order parameter.[4] At the same time, for transitions involving lattice distortion or magnetic ordering, the order parameter is the displacement of atoms or the magnetic moment. In the theories of CDW's and SDW's, the dielectric gap is proportional to them and hence formally acts as the order parameter. On the other hand, in a purely electronic MDT, e.g., in the Hubbard model, the dielectric gap cannot be *per se* the order parameter. The thorough theoretical treatment presented in Sec. 5 of this review shows that in this case one must consider the metallic phase to be ordered: the so-called metallic order parameter arises in the transition from the dielectric to the metallic phase.

Thus, for an MDT arising from the formation of CDW's and SDW's, the theory is restricted to calculating the electronic spectrum and its modification with variation of temperature, pressure, defect concentration, etc. The theory of such an MDT is close to the theories of other electronic phase transitions: the theories of superconductivity,[7,18,19] of the band theory of magnetism,[35,36] and the theory of an exciton dielectric.[7,28,37,38]

At the same time, for substances in which the transition is accompanied by structural or magnetic phase transitions, the theory of MDT's must include the corresponding aspects of the theory of structural and magnetic phase transitions.[35]

Moreover, in the MDT models involving formation of CDW's and SDW's, incommensurable phases[39] can arise under certain conditions, and they are being intensively

studied in other fields of solid-state physics.[40] However, the discussion of incommensurable phases lies outside the theme of this review.

A considerable majority of the transitions being discussed are first-order transitions, and critical fluctuational phenomena[41] apparently are not manifested; at least we know of no such examples (although the possibility of existence of a broad fluctuational region has been discussed theoretically in Refs. 42 and 43).

Owing to the brevity of this review, we have not adopted the aim of tracing in detail the history of the study of MDT's: one can find the information on the early studies in the cited reviews.[14-16,28-31] We point out also the book of Ref. 44 part of which is devoted to materials having MDT's. Hence the reference list makes no claim to completeness, and the references to the experimental results are given mainly for the recent studies.

## 2. FUNDAMENTAL MECHANISMS OF THE METAL-DIELECTRIC TRANSITION

### 2.1. Metal-dielectric transition in the Hubbard model

The Hamiltonian of the Hubbard model[24] includes the Coulomb repulsion $U$ of electrons by a single atomic s-orbital and the hopping (tunneling) of the electrons between atoms with the transport integral $t$ ($\mathbf{f} - \mathbf{f}'$):

$$\mathcal{H} = \sum_{\mathbf{f}, \sigma} \left[ (\varepsilon - \mu) n_{\mathbf{f}}^{\sigma} + \frac{U}{2} n_{\mathbf{f}}^{\sigma} n_{\mathbf{f}}^{-\sigma} \right] + \sum_{\mathbf{f} \neq \mathbf{f}', \sigma} t(\mathbf{f} - \mathbf{f}') a_{\mathbf{f}\sigma}^{+} a_{\mathbf{f}'\sigma}.$$

(1)

Here $n_{\mathbf{f}}^{\sigma} = a_{\mathbf{f}\sigma}^{+} a_{\mathbf{f}\sigma}$, $a_{\mathbf{f}\sigma}$ is the Fermi operator for annihilation of an electron at the node f having the spin projection $\sigma$ (in the Wannier representation), $\varepsilon$ is the energy of the atomic one-electron level, and $\mu$ is the chemical potential. The attractiveness of the Hubbard model lies in the fact that it includes two opposite limiting cases.

The *band limit* exists when $U \ll W$. In this case the Hamiltonian of (1) describes free electrons having the spectrum

$$\varepsilon(\mathbf{k}) = \varepsilon + t(\mathbf{k}) - \mu, \quad t(\mathbf{k}) = \sum_{\mathbf{h}} t(\mathbf{h}) \exp(i\mathbf{k}\mathbf{h}), \quad (2)$$

as calculated in the strong-coupling method. These electrons form an electron gas with a definite Fermi surface, metallic conductivity, and a temperature-independent Pauli paramagnetic susceptibility $\chi_0$. Usually one restricts the treatment to taking account of only the $Z$ nearest neighbors in calculating $t(\mathbf{k})$. Then we have $|t|Z = W$, where $W$ is the half-width of the band.

The *atomic limit* corresponds to $W \ll U$. Each atom has four states (for a nondegenerate model): the "hole" $|0\rangle$—a vacuum state without electrons having the energy $\varepsilon_0 = 0$, two single-electron states $|\sigma\rangle = a_{\mathbf{f}\sigma}^{+}|0\rangle$ with the spin projections $\sigma = \uparrow$ and $\sigma = \downarrow$ and the energy $\varepsilon$ and the "pair" $|2\rangle = a_{\mathbf{f}\uparrow}^{+} a_{\mathbf{f}\downarrow}^{+}|0\rangle$—a two-electron state with spin 0 and energy $2\varepsilon + U$. Such a system of isolated atoms is a dielectric with a paramagnetic susceptibility that obeys the Curie law $\chi = C/T$, where the quantity $C$ depends on the mean number of electrons per atom

$$\rho = \frac{1}{N} \sum_{\mathbf{k}, \sigma} \langle n_{\mathbf{k}}^{\sigma} \rangle.$$

Both of these limits and also the intermediate cases are obtained by varying the single dimensionless coupling constant $\lambda = U/2W$ from zero to infinity. When $\lambda \ll 1$, one can take account of the Coulomb interaction by the same methods as in the theory of a nonideal Fermi gas.[18] In particular, the Hartree-Fock corrections to the spectrum reduce to an inessential shift in the chemical potential. At the same time, the simplified form of the Coulomb interaction does not allow one to describe fully all the characteristic properties of metals. For example, the collective oscillations of the density of particles have a zero-sound spectrum, rather than a plasma spectrum.[45] This is a consequence of the $\delta$-function form of the potential.[46]

In the opposite limit one can also have a perturbation theory in terms of $\lambda - 1 \ll 1$; various approximate solutions have been discussed in Refs. 47–51 and in the earlier papers cited there. For the homopolar case $\rho = 1$, the main result of the perturbation theory in terms of $\lambda - 1$ reduces to the appearance of an effective exchange interaction of the Heisenberg type. This leads to antiferromagnetic ordering with the Néel temperature $T_N \sim t^2/U$. The single-particle transitions with energies $\varepsilon$ and $\varepsilon + U$ are smeared out into narrow Hubbard bands[16] separated by the gap $E_g = E_g(U, W) < U$, the Fermi level lies inside the dielectric gap, and the system remains a dielectric with the susceptibility $\chi = C/(T + T_N)$. The fundamental point is the difference of the statistics of the quasiparticles in the Hubbard band and in the band of electrons as calculated by any standard method of one-electron band theory. The total number of states in the band is two (per atom), and one in the Hubbard band. The spin-free character of the quasiparticles in the atomic limit has been noted in a number of studies (see, e.g., Ref. 52).

In the exact solution of the one-dimensional Hubbard model[53] and in the limit $T = 0$, no phase transition was found: when the number of electrons equals the number of nodes and when $\lambda \neq 0$, the system always remains antiferro-dielectric. As regards the three-dimensional case, it is intuitively clear that the metal-dielectric transition (in any case, at not too low a temperature) must occur in the region $\lambda \sim 1$, where perturbation theory is inapplicable. Just as in the theory of second-order phase transitions, one can escape the framework of perturbation theory into some particular variant of the self-consistent-field method.[25,27,54-58] A detailed analysis of the results obtained in this way is given in Sec. 5.

It can be shown that the restriction to only s-electrons strongly narrows the field of applicability of the Hubbard model, since an MDT in a system of s-electrons could occur only in systems of the type of solid hydrogen or helium.

In compounds with d-electrons, owing to orbital degeneracy, the number of possible states reaches $2^{10} = 1024$. However, owing to splitting of the d-levels in the crystal field, a situation can occur in which one d-level with an energy $\sim \varepsilon_F$ is split rather far from the remaining d-levels. This is equivalent to the Hubbard model (see, e.g., the structure of the bands of $VO_2$ and $V_2O_3$ proposed by Goodenough[59]).

In systems of cubic symmetry the crystal field splits the

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d-levels into groups of e- and t-states, in which respectively 4 and 6 electrons can lie. The situation with a half-filled band in compounds of the type of NiO and $NiS_2$–$e_g^2$ or VO–$t_{2g}^3$ has been studied in Ref. 25. The authors were able to find a spectrum of one-particle excitations with a gap at the Fermi surface and to determine the conditions for transition to the metallic state.

In the general case in which the mean number of electrons per atom in $n$, according to Pauling's principle of electroneutrality,[60] one can restrict the treatment to the three terms $E_n$, $E_{n-1}$, and $E_{n+1}$ corresponding to the ground states of the configurations $d^n$, $d^{n-1}$, and $d^{n+1}$. In the atomic limit the spectrum of one-particle excitations consists of two d-resonances $\Omega_- = E_{n-1} - E_n$, $\Omega_+ = E_{n+1} - E_n$, whose collectivization can be calculated by perturbation theory. In the atomic limit the width of the corresponding Hubbard bands is small in comparison with the spacing between them $\Omega_+ - \Omega_-$; the lower band is filled while the upper band is empty. That is, in its electrical properties such a model is equivalent to the nondegenerate Hubbard model. At the same time the magnetic properties can differ strongly, since the spins $S_n$, $S_{n-1}$, and $S_{n+1}$ can take on different values. Qualitative agreement with the Hubbard model occurs when $S_n = 1/2$, and $S_{n\pm1} = 0$.

### 2.2. Metal-dielectric transition with formation of an atomic or magnetic superstructure

A transition of this type, which is an analog of a Peierls transition in a one-dimensional system, and which involves formation of an exciton dielectric, arises every time that the electron and hole bands of a semiconductor having a small forbidden band[21] or a semimetal with a small overlap of bands[20] are congruent. If here the extrema of the electron and hole bands are separated by the wave vector $\mathbf{Q}$, the condensate of electron-hole pairs $\langle a_{1k\sigma}^+ a_{2k+Q,\sigma'} \rangle$ arising from interband interaction leads to appearance of a superstructure (whose period is determined by the vector $\mathbf{Q}$) and is accompanied by CDW's in the case of singlet pairing ($\sigma = +\sigma'$) and SDW's in the case of triplet pairing ($\sigma = -\sigma'$). The studies on the theory of an exciton dielectric and the problems involving the theory of superconductivity and structural phase transitions are reviewed in Refs. 7, 28, 37, and 38.

The single-band version of an exciton dielectric treated in Refs. 22 and 23 is more applicable for describing MDT's in narrow-band compounds. It was shown in these studies that, if the energy of the band electrons for all wave vectors $\mathbf{k}$ satisfies the so-called nesting condition

$$\varepsilon(\mathbf{k} + \mathbf{Q}) = -\varepsilon(\mathbf{k}), \qquad (3)$$

then the metallic state with a half-filled band (for the case in which $2\mathbf{Q}$ coincides with one of the reciprocal-lattice vectors) is unstable, and the transition to a dielectric phase is accompanied by appearance of an intraband electron-hole condensate.

Instability with respect to formation of CDW's is determined by the condition of appearance of a purely imaginary pole in the dielectric permittivity $\varepsilon(\mathbf{Q}, \omega)$. Since the renormalization of the phonon frequencies is determined by the same graphs of perturbation theory that are summed in calculating $\varepsilon(\mathbf{Q}, \omega)$, then a purely imaginary pole simultaneously arises in the phonon Green's function.[23] That is, the formation of CDW's is accompanied by a structural transition with formation of a superstructure.

Analogously the instability with respect to SDW's is determined by the condition of appearance of a purely imaginary pole in the magnetic susceptibility and is accompanied by the appearance of a magnetic superstructure with the wave vector $\mathbf{Q}$. The model of a MDT involving antiferromagnetic ordering was first treated by Slater.[17] One of the first studies on SDW's was that of Overhauser.[61] The theory of SDW's is also applied to describe antiferromagnetism in chromium and other band antiferromagnetics, as has been reflected in a recent review.[62]

The condition (3) physically implies the presence of planar regions of the Fermi surface, and it arises for spectra calculated, e.g., in the strong-coupling method, for a certain lattice symmetry and a certain electron concentration. For the one-dimensional case $\varepsilon(\mathbf{k}) = -W \cos ka$, this condition arises at any concentration and leads to the well-known Peierls instability.[12] In the strong-coupling method, condition (3) can hold only for alternate lattices, which are subdivided into two equivalent sublattices, such that each node of the A-sublattice is surrounded only by nearest neighbors from the B-sublattices, and vice versa. In particular, they include the three-dimensional simple cubic and bcc lattices, where the condition (3) is satisfied for a half-filled band. The Fermi surface for the spectrum in a simple cubic lattice

$$\varepsilon(\mathbf{k}) = \varepsilon - \frac{W}{3}(\cos k_x a + \cos k_y a + \cos k_z a) - \mu \qquad W = 6|t| \qquad (4)$$

for $\rho = 1$, when $\mu = \varepsilon$, has the form of a cube. The nesting condition is also satisfied for a bcc lattice with $\rho = 1$:

$$\varepsilon(\mathbf{k}) = \varepsilon - W \cos \frac{k_x a}{2} \cdot \cos \frac{k_y a}{2} \cdot \cos \frac{k_z a}{2} - \mu, \qquad W = 8|t|.$$

The order parameters are the relative displacement of the atoms of the sublattices, which is proportional to the singlet gap $\Delta_s$ for CDW's, and the magnetization of the sublattice $R$, which is proportional to the triplet gap $\Delta_t$ for SDW's. The equation for the gap coincides in form with the well-known Bardeen-Cooper-Schrieffer (BCS) equation from the theory of superconductivity[19] and it yields for $T = 0$

$$\Delta_{i0} = 2W \exp\left(-\frac{1}{\lambda_i}\right), \qquad \lambda_i = g_i N(0) \quad (i = s, t). \qquad (5)$$

Here $N(0)$ is the density of states at the Fermi level, $g_s$ and $g_t$ are the singlet and triplet coupling constants, and the coefficient 2 in front of $W$ corresponds to a rectangular density of states.

The modification of the spectrum (4) involving, e.g., taking account of hopping of an electron to non-nearest adjacent nodes, substantially affects the results, and is especially important for a bcc lattice, where the difference in distances between the first and second neighbors is small.
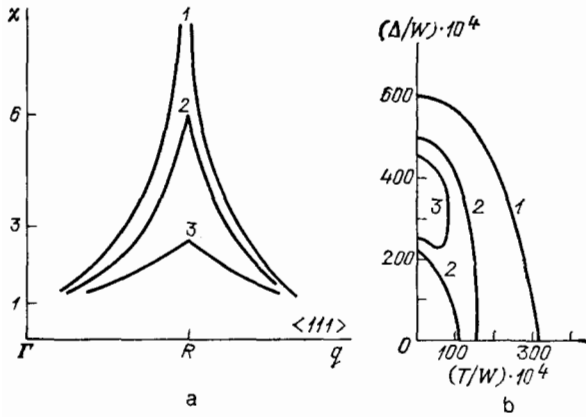
FIG. 1. Stabilization of the metallic phase taking into account hopping between non-nearest neighbors. a—Generalized susceptibility $\chi(\mathbf{q}, 0)$ for the different values of $\varphi/W = 0$ (1), 0.2 (2), and 0.4 (3). b—Temperature-dependence of the gap $\Delta$ for $\varphi/W = 0.03$ with $\lambda^{-1} = 3.50$ (1), 3.70 (2), and 3.80 (3); for $\lambda^{-1} > 4.11$ the gap equals zero at all temperatures.

For example, for a simple cubic lattice the addition to the spectrum (4)

$$\delta\varepsilon(\mathbf{k}) = \varphi\,(\cos k_x a \cdot \cos k_y a + \cos k_y a \cdot \cos k_z a + \cos k_z a \cdot \cos k_x a)$$

models the Fermi surface, which is now determined by the equation

$$\varepsilon(\mathbf{k}) + \delta\varepsilon(\mathbf{k}) = 0. \qquad (6)$$

As was shown in Ref. 23, the self-consistency equation in this case acquires a more complex form than in the BCS theory:

$$\lambda_t^{-1} = \frac{1}{2}\int_0^W \frac{d\varepsilon}{(\varepsilon^2 + \Delta_t^2)^{1/2}}\left\{ \text{th}\left[\frac{(\varepsilon^2 + \Delta_t^2)^{1/2} + \varphi}{2T}\right] \right.$$
$$\left. + \text{th}\left[\frac{(\varepsilon^2 + \Delta_t^2)^{1/2} - \varphi}{2T}\right]\right\} \qquad (7)$$

and it has two nontrivial solutions at $T = 0$. When $\varphi < \Delta_0$, the solution of (7) is $\Delta = \Delta_0$, and when $\Delta_0/2 < \varphi \leqslant \Delta_0$, the new solution $\Delta_1 = [\Delta_0(2\varphi - \Delta_0)]^{1/2} \leqslant \Delta_0$ appears.

Comparison of the thermodynamic potentials of the dielectric and metallic $M$ phases shows that the phase $\Delta_1$ is not realized at $T = 0$.[23]

The solutions of Eq. (7) at finite temperatures are shown in Fig. 1, from which we see that a critical point $\varphi_0$ appears. It is of a type such that, when $\Delta_0/2 < \varphi < \varphi_0$, the transition remains continuous, while when $\varphi_0 < \varphi < \Delta_0$, a jump in the order parameter appears.[63] It was shown here also how the modulation of the Fermi surface removes the singularity in the generalized susceptibility $\chi(\mathbf{Q}, 0)$, which leads to instability with respect to doubling of the period.

Other factors that lead to a first-order transition can be: a) interactions that fix the phase of the order parameter[64]; b) terms cubic in $\Delta$ in the free energy of the system arising from taking account of collective oscillations[37,65] or anharmonicity[66]; c) a sharp change in the correlation energy near the MDT point.[41]

The band of electrons (2) is split after doubling of the period into two subzones:

$$E^{\pm}(\mathbf{k}) = \varepsilon \pm (t^2(\mathbf{k}) + \Delta^2)^{1/2} - \mu\,. \qquad (8)$$

The gap between the latter is determined by the solution of Eq. (7). The phonon spectrum is also rearranged, with doubling of the number of branches in it.[23,28] Going outside the framework of the generalized Hartree-Fock approximation (GHFA) enables one to find the decay of the phonons in the dielectric phase[67] caused both by electron-phonon and phonon-phonon interactions.

We note that most studies on MDT's involving the formation of CDW's and SDW's have been conducted within the framework of the GHFA, which differs from the ordinary Hartree-Fock approximation in taking account of the "anomalous" means $\langle a_{\mathbf{k},\sigma}^{+} a_{\mathbf{k}+\mathbf{Q},\sigma'}\rangle$. Actually this is the weak-coupling approximation $\lambda_s \ll 1$ and $\lambda_t \ll 1$. The latter condition implies that the system exists in the metallic state far from the Mott-Hubbard transition point $\lambda_t \sim 1$.

The Fermi-liquid treatment is applicable for such a system when conducted with allowance for electron-hole pairing.[68] It confirms the conclusion[69] that CDW's and SDW's cannot coexist for the half-filled band of (3) or in the two-band model of an exciton dielectric with equal numbers of electrons and holes. Singlet and triplet pairing can coexist, e.g., upon doping. This leads to the appearance of exciton paramagnetism.[37]

### 2.3. Metal-dielectric transition with change in the topology of the Fermi surface

Let us assume that the Fermi level of noninteracting electrons lies in the region of overlap of two allowed bands. Their mutual arrangement can vary owing to variation of the lattice parameters under pressure, upon doping, or upon thermal expansion. Consequently a complete separation of the bands can occur, while the Fermi level can lie inside the dielectric gap. According to Ref. 70, a transition of this type at $T = 0$ is a 2.5-order transition, since the thermodynamic potential depends on the volume according to the "five halves" law:

$$\delta\Omega \infty |V - V_c|^{5/2}.$$

This weak dependence is smeared out by the temperature, and hence such a transition at $T \neq 0$ is not, strictly speaking, a phase transition.[70]

The fundamental conclusions obtained in the model of noninteracting electrons continue to hold when we take account of Fermi-liquid effects.[71] However, taking account of the long-range component of the Coulomb interaction (according to perturbation theory) led the authors of Ref. 72 to conclude that the singularities of the thermodynamic potential are amplified near the transition point.

### 3. BAND THEORY OF THE METAL-DIELECTRIC TRANSITION WITH FORMATION OF CHARGE- OR SPIN-DENSITY WAVES

The experimental study of compounds that undergo a metal-dielectric transition enables their classification into two groups in terms of the temperature-dependence of the paramagnetic susceptibility $\chi(T)$ in the metallic high-tem-

perature region. For example, the temperature-dependence of $\chi(T)$ for $VO_2$ and NiS is fundamentally of the Pauli type. At the same time, the susceptibility of $V_2O_3$ has a Curie-Weiss behavior (see, e.g., Ref. 16). We can naturally assume[55] that such a classification corresponds to substances with weak ($\lambda \ll 1$) and intermediate ($\lambda \sim 1$) electron-electron correlations. We note that the self-consistent-field theory presented below in Sec. 5 confirms the possibility of classifying metals into two categories—those having localized magnetic moments or not (and correspondingly obeying the Curie law or not in the paraphase). However, no consistent theory exists at present that goes outside the framework of the self-consistent-field method and can describe the transition region from localized to delocalized moments.

Section 3 will study substances with a rather weak correlation, which can be taken into account within the framework of the GHFA. A detailed discussion of the physical properties and mechanisms of the MDT's of the vanadium oxides is given in the book of Ref. 5.

### 3.1. The transition in vanadium dioxide

None of the compounds discussed below has a simple cubic or bcc lattice that would allow using the condition (3) for the d-bands. At the same time, they all have a distinct symmetry axis (the c-axis), along which chains of cations lie. Therefore a number of studies have assumed that a fraction of the d-bands is quasi-one-dimensional and satisfies the condition (3) with $\mathbf{Q} = (0, 0, \pi/c)$, where $c$ is the distance between the cations in the chain (for $VO_2$, Refs. 73–76 for $V_2O_3$, Refs. 59, 77–78 and for NiS Refs. 79, 80). However, a metallic phase with a quasi-one-dimensional conduction band would have a considerable anisotropy of all the electronic properties. This is actually not observed. Hence we can assume that the Fermi level intersects two bands—one band singular in the sense of the condition (3) and the second nonsingular and formed by hybridized orbitals and having a complicated three-dimensional dispersion law.

Such a model has been proposed for $VO_2$.[75] A band calculation[81] has confirmed it in the main (see Fig. 2). However the vector $\mathbf{Q}$ for $VO_2$ proved to be equal to $\pi(1/a, 0, 1/c)$. A calculation of the generalized susceptibility showed the existence of a maximum of $\chi(\mathbf{Q}, 0)$ at $Q = (\pi/a, 0, \pi/c)$.[81] This leads to phonon instability and the formation of CDW's. Experimental study of the electronic structure of $VO_2$ by optical and thermooptical methods also confirms the association of the MDT with electron-phonon interaction.[82]

Figure 3 shows the possible states of the two-band model. A self-consistent theory of the MDT in the two-band model[63] has been constructed with account taken of the two types of anomalous means—singlet and triplet. The spec-
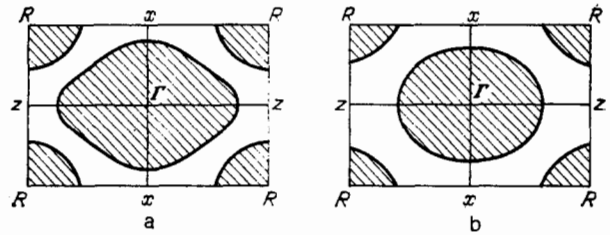


FIG. 2. Cross sections of the Fermi surface for two bands of $VO_2$ that intersect the Fermi level.[81]

trum of the electrons of band 1 with spin up or down is

$$E_1^\pm(\mathbf{k}) = \bar{\varepsilon} \pm (t_1^2(\mathbf{k}) + \Delta_\sigma^2)^{1/2} + \delta\varepsilon_1(\mathbf{k}). \quad (9)$$

In the case of only singlet or only triplet pairing, the gaps are the same: $|\Delta_\uparrow| = |\Delta_\downarrow|$. If CDW's and SDW's coexist, then the spin degeneracy is removed,[37] $|\Delta_\uparrow| \neq |\Delta_\downarrow|$. One seeks the gap $\Delta_\uparrow$ and $\Delta_\downarrow$ and the chemical potential $\mu$ from the system of self-consistency equations. In the multiband model the latter differs from the equations of Ref. 37 in the presence of a reservoir of electrons of finite capacity. The singlet and triplet anomalous means are found as the symmetric and antisymmetric linear combinations:

$$\Delta_s = \frac{1}{2} |\Delta_\uparrow + \Delta_\downarrow|, \quad (10)$$

$$\Delta_t = \frac{1}{2} |\Delta_\uparrow - \Delta_\downarrow|. \quad (11)$$

The important parameters of the two-band model are the spacings between the energy centers of gravity of the bands $\varepsilon_2 - \varepsilon_1 = d$, which is determined for $VO_2$ by the splitting of the $t_{2g}$ level by the tetragonal component of the crystal field, and also the relationship between $d$ and the band widths $2\lambda W$. The Fermi level intersects both bands in the metallic phase if $W_2 > d$. In the converse case the second band is empty and plays no role.

To describe the MDT's in stoichiometric $VO_2$ and $NbO_2$, one must seek the singlet solution $\Delta_\uparrow = \Delta_\downarrow = \Delta$ for the concentration of electrons $\rho = 1$. Under the conditions $T = 0$ and $\varphi = 0$ and for the semielliptical-band model of (27), the energy gap is

$$\Delta(0) = \frac{4}{e} W_1 \exp\left(-\frac{1}{\lambda_s}\right), \quad \lambda_s = g_s N_1(0). \quad (12)$$

The results of numerical calculation for $T \neq 0$ and $\varphi \neq 0$ are shown in Fig. 4, from which we see that two nontrivial solutions exist, $\Delta_1 > \Delta_2$. Comparison of the thermodynamic potentials of these phases and the metal phase $\Delta = 0$ shows that the phase $\Delta_2$ is unstable at $\rho = 1$. A first-order MDT occurs with increasing $T$ with $T_c \ll \Delta(0)$ and a jump in the gap $\Delta(T_c)/\Delta(0) \sim 1$. At the transition point we have
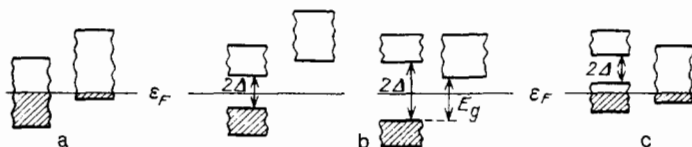


FIG. 3. Possible states of the two-band model of $VO_2$ with band 1 satisfying the nesting condition. a—Metal. b—Variants of a dielectric. c—Semimetal.
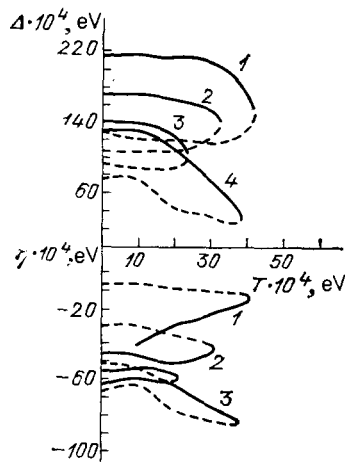
FIG. 4. Temperature dependences of the gap $\Delta$ and the chemical potential $\eta$ for $\lambda^{-1} = 3.50$. $W_1 = 0.5$ eV, $W_2 = 0.7$ eV, $d = 0.69$ eV, $\varphi = 0.15$ eV. Curves $1$–$4$ correspond to the values $\rho = 1$ ($1$), $0.990$ ($2$), $0.982$ ($3$), and $0.980$ ($4$). The solid lines pertain to the phase $\Delta_1$, and the dotted lines to the phase $\Delta_2$.



FIG. 5. Phase diagram of the two-band model. Solid line—magnetic field $H = 0$, dotted line—$\mu_B H = 0.001$ eV, dot-dash line—$H = 0$, $W_2 = 0.705$ eV; see Fig. 4 for the rest of the parameters.

$\mu(\Delta_1) = \mu(\Delta_2) = \mu(0)$. For $\varphi = 0$, the solution of the equations yields a second-order transition with $T_c \sim \Delta(0)$.

The physical mechanism that yields a first-order transition when $\varphi \lesssim \Delta(0)$ is as follows. For $\rho = 1$, the dielectric gap in the spectrum (9) is $\Delta - \varphi$. If we have $\Delta_1(0) > \varphi$ when $T = 0$, then the quantity $\Delta_1(T)$ declines with increasing $T$ until the condition $\Delta_1(T_c) = \varphi$ is no longer satisfied. With further increase in $T$, the spectrum becomes semimetallic. If $\varphi \sim \Delta_1(0)$, then we have $T_c \ll \Delta_1(0)$, and we can neglect the thermal excitation of electrons through the gap. In this case the carriers arise jumpwise at $T_c$. Actually we see from curve $1$ in Fig. 4 that $\Delta_1(T_c) = \varphi$. For small $\varphi$, the intersection of $\Delta_1(T)$ with the level $\varphi$ occurs at $T \sim \Delta_1(0)$, when the thermal scatter is substantial—in this case the concentration of carriers varies smoothly.

The two-band theory[63] also enabled understanding the existence of the triple points on the phase diagram of $VO_2$ doped with trivalent impurities (see Ref. 5 and the experimental studies cited there). Each $Me^{3+}$ atom in the compound $V_{1-x}Me_x^{3+}O_2$ leads to formation of a hole on the background of $V^{4+}$ ions, and the concentration of electrons decreases.

The small concentrations at which the new phases and the triple point ($x_c \sim 0.01$) were found in $V_{1-x}Me_x^{3+}O_2$, and also the identical phase diagrams upon doping with an atom of either a transition or a nontransition element have allowed one to assume that these phases also exist in stoichiometric $VO_2$, but in a metastable state.[83] This assumption is confirmed in experiments on uniaxial pressure, in which the dielectric monoclinic phase that is metastable under normal conditions is separated out in a stable modification.[84]

For small $x$ it is reasonable to use the rigid-band approximation for the metal phase, while assuming that none of the parameters of the substance vary except the concentration.

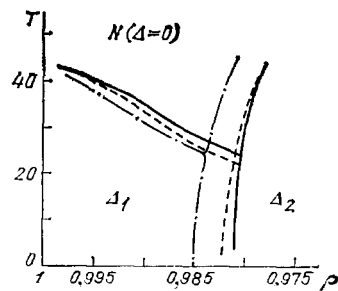There is also an indirect experimental proof of the applicability of the rigid-band approximation, which was obtained in studying $V_{1-x-y}Me_x^{3+}Mo_yO_2$.[85] Each Mo ion furnishes an extra electron and thus compensates holes created by $Me^{3+}$. Consequently $\rho$ increases, while experimentally[85] the M2 phase stable in the absence of Mo ($\Delta_2$ in our notation) is replaced by the M1 ($\Delta_1$) phase as $y$ increases.

Curves $2$–$4$ in Fig. 4 correspond to an increased concentration of holes. The result of solving the system of self-consistency equations for $\rho < 1$ shows that the phase $\Delta_2$ is stabilized with decreasing $\rho$ with a smaller gap, while a triple point and a region of stability of a new phase arise in the phase diagram in the ($\rho$, $T$) plane (Fig. 5).[29] All the boundaries in Fig. 5 are first-order transition lines. As we see it, the leftward shift of the triple point with increasing $W^2$ imitates the stabilization of the $\Delta_2$-phase upon uniaxial compression perpendicular to the $c$ axis. The effect of different pressures on the triple point has been studied in Ref. 86. Figure 5 also shows the shift of the triple point in a strong magnetic field, while $T_c$ practically does not vary upon imposing a magnetic field.

Thus the rigid-band model for the metal phase of $V_{1-x}Me_x^{3+}O_2$ enables one to describe the low-temperature phases qualitatively correctly. However, a more exact description of the phase diagram must include, e.g., taking account of the scattering of electrons by the random potential of the impurities, the variation of the parameters of the band structure upon doping, etc.

Moreover, actually the symmetries of the M1 and M2 phases differ in the method of pairing of the cations.[5] In the simplified model[63] with one cation, these phases have an identical symmetry of the displacements of the cations, while differing only in the values of $\Delta_1$ and $\Delta_2$. For this same reason an intermediate $T$-phase is lacking in the theory between the M1 and M2 phases. The electric and magnetic properties of doped $VO_2$ have been discussed in Refs. 5, 16, and 87 on the basis of a model of quasi-one-dimensional Heisenberg spin chains and formation of spin-polarons.

The problem is interesting of the need for long-range crystalline order for the existence of an MDT in $VO_2$. The experimental studies contain contradictory results: according to Ref. 88, a dielectric phase in amorphous $VO_2$ is absent, and crystalline order is necessary for existence of an MDT. However, according to Ref. 89, a transition is observed in the amorphous state. Apparently the difference involves a dif-

fering degree of amorphousness. Structural and electric measurements[90] have shown that the MDT in an amorphous specimen prepared by cooling from the melt is conserved, although $T_c$ and the magnitude of the jump in conductivity are decreased. At the same time, the degree of amorphousness of the prepared specimens was not studied specially, and the diffuseness of the diffraction lines in the x-ray spectra enabled the authors[90] to speak "rather of a strongly defective structure of $VO_2$ than of total absence of structure."

Another example of the influence of disorder on an MDT is given by doping with quadrivalent impurities, e.g., in the system $V_{1-x}Nb_xO_2$ an MDT was observed up to $x \lesssim 0.15$,[91] in $V_{1-x}Mo_xO_2$ up to $x \lesssim 0.2$.[92] In Ref. 93 the influence was studied of two types of disorder: diagonal in the node representation and nondiagonal (interatomic), on the MDT with formation of CDW's. Diagonal disorder suppresses the dielectric phase just like charged impurities in an exciton dielectric[94] and paramagnetic impurities in a superconductor.[95] Nondiagonal disorder alters the width $W$ of the band, thus affecting the magnitude of $\Delta(0)$ and $T_c$ [see (12)]. Both an increase and a decrease are possible, depending on the sign of the change.

In the case of replacement of vanadium ions by ions of a 4d-metal whose ionic radius is larger, we have $\delta W > 0$, and the decrease in $T_c$ owing to diagonal disorder is partially compensated by an increase owing to nondiagonal disorder. At the same time, in the replacement of a 4d-ion by a 3d-ion, we have $\delta W < 0$, and both forms of disorder decrease $T_c$. The former case is characteristic of the systems $V_{1-x}Nb_xO_2$ and $V_{1-x}Mo_xO_2$ cited above,[5,91,92] where the slow decline in $T_c$ can apparently be explained by partial compensation of the contributions of diagonal and nondiagonal orders. The latter case corresponds to the system $Nb_{1-x}Ti_xO_2$, in which all the disorder mechanisms act toward decreasing $T_c$: one observes a sharp decrease in $T_c$ from the value 1090 K at $x = 0$ to 300 K at $x = 0.017$.[96]

Thus far we have been discussing $VO_2$ from a single standpoint, namely that of bands, in which the very major effects of Coulomb and electron-phonon interactions are associated with the singling out of the anomalous singlet and triplet means. We must acknowledge that a number of experiments[5] exists for which the interpretation in the language of Mott-Hubbard correlations seems preferable.[16] Apparently, $VO_2$ is characterized by an intermediate situation, in which the correlations are not so large as, e.g., in $V_2O_3$, but neither are they small enough, so that the correlation corrections to the Hartree-Fock approximation are substantial.

### 3.2. The metal-dielectric transition in nickel sulfide

Despite the large number of theoretical and experimental studies (see the reviews of Refs. 15, 16, 28–31), the nature of the ground state and the MDT in NiS were unclear for a long time. Most of the investigators started with the fact that the high-temperature phase of NiS is a paramagnetic metal with band-type conduction and an almost temperature-independent Pauli susceptibility,[97,98] and that the transition point coincides with the Neél temperature $T_c = T_N = 264$ K.

Two sets of experimental data on the temperature-dependence of the electric conductivity below $T_c$ contradict one another: according to Ref. 97, NiS is a semiconductor with a large anisotropy of the conductivity $\sigma_\perp/\sigma_\parallel \sim 10^2$, while according to Ref. 98 it is a semimetal with a small anisotropy of conductivity.

A calculation of the band structure of NiS[99,100] has shown that the Fermi level $\mu$ intersects several bands: the narrow d-band (mainly formed by the $e_g$-states of Ni) and sp-$t_{2g}$-hybridized bands of sulfur and nickel, with $\mu$ lying near the center of the d-band (band 1) and near the top of the sp-$t_{2g}$-band (band 2). These calculations confirmed the qualitative two-band model of the metallic phase.[97,98]

The symmetry of the $e_g$-functions and the arrangement of the cations in NiS (chains along the hexagonal c-axis) are of a type such that the overlap of the $e_g$ orbitals occurs mainly along the c-axis. Hence we can expect the nesting condition to be satisfied with $Q = (0, 0, \pi/c)$. Actually, taking account of the exchange molecular fields involving the alternation of spins along the c-axis in the band calculations[100] showed that the formation of SDW's leads to an MDT.

It was noted also in Refs. 17 and 18 that antiferromagnetic ordering can lead to formation of a dielectric gap; a self-consistent theory for SDW's of the states was developed in Ref. 21. The two-band theory described above allows one to explain the apparent experimental contradictions between Refs. 97 and 98 upon taking account of the antisymmetric solutions $\Delta_\uparrow = -\Delta_\downarrow = \Delta$ corresponding to SDW's.

As will be shown below (see also Refs. 32 and 100), the reason for these contradictions is explained by the presence of cation vacancies. In an ideal, stoichiometric NiS crystal the ground state is of semiconductor type. However, a semimetallic phase is formed with increasing number of cation vacancies.

From the formal standpoint, the transition from singlet to triplet solutions consists in replacing the coupling constants $g_s \rightarrow g_t$. Hence the results[63] described above for $VO_2$ can be obtained also for NiS, namely, the jumpwise character of the transition, and also the existence of additional ordered phases and of a triple point in the phase diagram.

Since band 2 in NiS intersects $\mu$ near the top (but in $VO_2$ near the bottom), it is convenient to alter the notation: now let $\varepsilon_2$ be the top of band 2, and $\varepsilon_1$ as before be the center of band 1, and let $d = \varepsilon_2 - \varepsilon_1$. The stoichiometric composition of NiS corresponds to one hole per cell, $\rho_h = 1$. We assume for simplicity that both bands are nondegenerate,[2] and then $\rho = 3$ for $\rho_h = 1$. As is known, like other monosulfides of 3d-metals, NiS practically cannot be made stoichiometric. Usually compositions close to stoichiometric contain excess sulfur and a cation deficiency. This gives rise to excess holes ($\delta\rho < 0$).

We shall take account of the smooth modification of the Fermi surface involving deviation from the condition (3) owing to non-nearest neighbors in the same way as in Refs. 23 and 63 by assuming that $\delta\varepsilon_1(k) = \varphi$ in one half of the solid angle of each octant of the surface, and $\delta\varepsilon_1(k) = -\varphi$
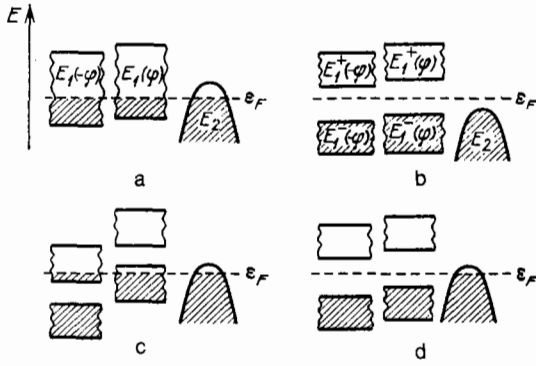
FIG. 6. Band diagram for NiS. a—Metal. b—Proper semiconductor. c—Semimetal. d—p-type semiconductor.

in the other half. Then the band model of the metallic phase of NiS will look as shown in Fig. 6.

For the proper semiconductor that arises below $T_c$, in the stoichiometric case ($\delta\rho = 0$), the chemical potential lies inside the gap, and the SDW amplitude $\Delta = \varphi \langle \sigma^z \rangle$ in the model of a rectangular density of states $N_\lambda (\varepsilon) = (1/2) W_\lambda$ is equal at $T = 0$ to

$$\Delta_0 = \frac{W}{\mathrm{sh}\, \lambda_t^{-1}}. \tag{13}$$

This solution can occur when $\varphi + d < \Delta_0$. The magnetization of the sublattice is

$$\langle \sigma^z \rangle = \frac{\Delta_0}{4W_1} \mathrm{arsh}\, \frac{W_1}{\Delta_0}. \tag{14}$$

With a small concentration of holes $\delta\rho < \delta\rho_0 = (d + \Delta_0 - \varphi)/W_2$, they lie only at the top of band 2 (Fig. 6d), and the occupancy of the subbands $E_1^\pm (\pm\varphi)$ is not changed. Hence we have $\Delta = \Delta_0$, while the chemical potential is diminished. When $\delta\rho = 0$ the semiconductor phase is energetically more favored than the metallic phase $\Delta = 0$. However its stability decreases with increasing $|\delta\rho|$, and as a calculation of the energies of all the phases shows, when we have

$$|\delta\rho| > \delta\rho_1 = \frac{\Delta_0^2}{6W_1^2} + \frac{\varphi^2}{3W_1^2} + \frac{d}{W_1}$$

the metallic state becomes more favored. A semimetallic solution can also occur when $\mu$ also intersects the subbands $E_1^+ (-\varphi)$ and $E_1^- (\varphi)$ (Fig. 6c). In this phase (for simplicity we assume that $W_1 = W_2 = W$) the gap is equal to

$$\Delta_1 = \Delta_0 \{2\varphi\, [\Delta_0^2 + (d - W|\delta\rho|)^2]^{-1/2} - 1\}^{1/2} \tag{15}$$

and it increases linearly for small $|\delta\rho| \ll 1$. Comparison of the energies shows that the semimetallic phase is unstable in the stoichiometric case but is stabilized when $|\delta\rho| > \delta\rho_2$. An explicit expression for the critical concentration $\delta\rho_2$ is given in Ref. 101. The essential point is that $\delta\rho_2 < \delta\rho_1 < \delta\rho_0$. Hence in a stoichiometric specimen and when $|\delta\rho| < \delta\rho_2$, the ground state of NiS will be a semiconductor, but a semimetal when $|\delta\rho| > \delta\rho_2$. Apparently the difference between the results of Refs. 97 and 98 involves a different degree of nonstoichiometry of the specimens.

The two-band theory[80,101] also allowed one to relate the optical, electric, and magnetic data on NiS. Experiments on infrared absorption[102] revealed two gaps—a smaller one of 0.14 eV and a larger one of 0.4 eV. In our notation we have

$$\left.\begin{array}{l} E_{1\,\mathrm{min}}^+ (-\varphi) - E_{2\,\mathrm{max}} = 0{.}14\ \mathrm{eV}, \\ E_{1\,\mathrm{min}}^+ (-\varphi) - E_{1\,\mathrm{max}}^- (\varphi) = 0{.}4\ \mathrm{eV}. \end{array}\right\} \tag{16}$$

According to the magnetic and neutron-diffraction data,[98] the MDT in NiS is a sharply marked first-order transition with a practically temperature-independent magnetic moment ($\mu = (1.66 \pm 0.08)\mu_B$ at 4.2 K and $(1.50 \pm 0.10)$ $\mu_B$ at 260 K). Hence we can replace $\Delta(T)$ in the relationships (16) by $\Delta_0$. We obtain another equation for the three quantities $\Delta_0$, $\varphi$ and $d$ from the activation energy of conduction $E_g = 0.34$ eV.[97] In a substance with an anisotropic Fermi surface, the optical gaps that are sensitive to the anisotropy will not equal the activation energy of conduction, which is determined by quantities averaged over the Fermi surface. Hence, instead of all four of the subbands $E_1^\pm (\pm\varphi)$, two remain after averaging $E_1^\pm (0)$ having $\varphi = 0$, and then we have $E_g = \varphi_0 - d$. Consequently we find from the optical and electric data $\Delta_0 = 0.4$ eV, $\varphi = 0.2$ eV, and $d = 0.06$ eV, and we can calculate the magnetic moment of the sublattice by using (14). Recalling the twofold degeneracy of band 1, we have $\mu = 2g \langle \sigma^z \rangle \mu_B = 1.68\ \mu_B$ (the bandwidth is $2W = 1$ eV, according to Ref. 97). This agrees very well with the experimental data presented above.

The large anisotropy of the semiconductor phase found in Ref. 97 is explained by the presence of holes at the top of band 2, so that carriers exist in the basal plane, but are absent along the hexagonal axis. In the semimetallic phase carriers exist in all bands, and hence the anisotropy is small.

At the same time, a number of experimental facts cannot be explained within the framework of the two-band theory.[80,101] The fundamental ones are the structural data: the change in the lattice parameters and in the unit-cell volume—and also the softening of the phonon spectrum.[103,104] We should note that the distortion of the lattice in the MDT in NiS does not at all resemble the distortion of the lattices of $VO_2$, $V_2O_3$, CrS, and FeS, where the period along the $c$-axis is doubled. In NiS the cation sublattice is not distorted, and only the anions are displaced.

Another unsolved problem is the Néel temperature in NiS. Most investigators assume that $T_N = T_c$, and that the substance is paramagnetic in the metallic phase. However, Mott[16] assumes that $T_N \gtrsim 1000$ K. This statement is based on singling out the Curie-Weiss contribution to the temperature-dependence of the susceptibility. However, for NiS the deviations of $\chi(T)$ from the Pauli law are small, and the degree of accuracy of the description of these deviations from the Curie-Weiss law is unknown.[16] Moreover, as is known, the Coulomb correlations can lead to a temperature-dependence of $\chi(T)$ in paramagnetic materials.[26,105] A final answer to the problem of the magnetic properties of the metallic phase requires further studies.

### 3.3. The transition in vanadium sulfide

Just like the other monosulfides of 3d transition metals, VS is usually nonstoichiometric, and this nonstoichiometry

leads to a certain ambiguity in the experimental data. The final phase diagram in the composition-temperature plane has not yet been established. However, a region has been revealed near the stoichiometric composition where the MDT is accompanied by a structural transition.[106]

The band structure and the Fermi surface of the high-temperature hexagonal phase of VS have been calculated in Refs. 107 and 108, where the Fermi level was shown to intersect the partially filled d-bands. The Fermi surface has a rather complicated form. In particular, there is an electron cylinder near the center of the Brillouin zone (point $\Gamma$) and a hole cylinder near the point $M$ at the edge of the zone. The cylinders have an almost identical form and match rather exactly upon translation by the vector $Q$ in the $\Gamma M$ direction.

A theory of the MDT with formation of CDW's for VS was constructed in Ref. 109, which took account of only the singular regions of the Fermi surface (the electron and hole pockets). The theory[107–109] qualitatively explains the relation between the MDT and the structural distortion, as well as a number of other experimental data: the decrease in the Knight shift, the electronic susceptibility, the anomaly in the heat capacity, and the kinetic characteristics.

At the same time, the Knight shift does not drop to zero below $T_c$, but only by 30%; the temperature-dependence of the conductivity is not activational in type, as must happen in a semiconductor phase with a gap $2\Delta$ equal to 0.3 eV[109]; the Pauli susceptibility calculated in Ref. 107 is an order of magnitude smaller than the experimental value. All these discrepancies of the theory[109] with experiment primarily indicate the need for taking account of the other bands having nonsingular Fermi surfaces, the existence of which is implied by the band calculations.[107] A very simple possible three-band model includes two singular bands (an electron and a hole band) and one nonsingular band.[106] The Fermi level above $T_c$ intersects all three bands, while below $T_c$ it intersects only the third one. Then the density of states $N(\mu) \neq 0$ both above and below $T_c$, and the Knight shift does not fall to zero. The conductivity in this model is described by the formula

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_g}{T}\right) + \sigma_3(T).$$

Here $\sigma_3(T)$ is the conductivity in the third (nonsingular) band, which is not activational in type. The susceptibility in this model is also larger owing to the increase in the density of states at the Fermi level.

Actually the third band plays the role of a reservoir of electrons. Owing to the nonstoichiometry, the Fermi level is shifted, and in this case CDW's and SDW's of the phases can coexist. Depending on the relationship between the phases of the SDW's and CDW's in the coexistence region, the substance will be either antiferromagnetic with a distorted lattice or an "exciton ferromagnetic material."[37,69] The experimental data do not yet allow one to distinguish the region of coexistence of CDW's and SDW's of the phase. This will require further magnetic studies of different compositions of $V_{1-x}S$.
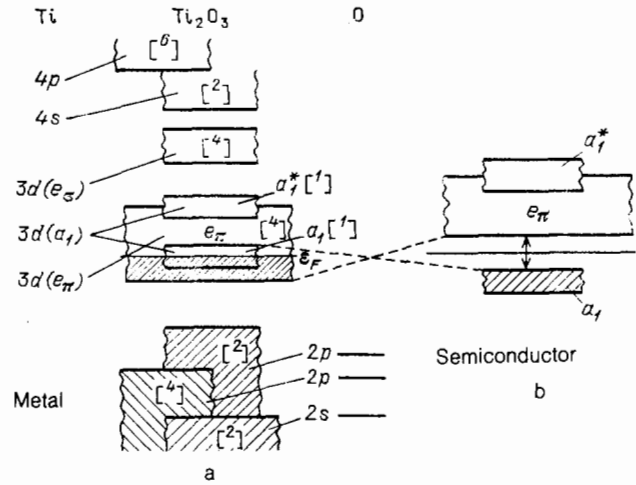


FIG. 7. Diagram of the band structure of $Ti_2O_3$ in the metallic (a) and semiconductor (b) phases.

## 3.4. The metal-dielectric transition in $Ti_2O_3$

The transition in $Ti_2O_3$ differs appreciably from the MDT in the vanadium oxides in the absence of a sharp jump in the electrical conductivity and in the absence of a marked transition point. The conductivity varies smoothly by a factor of 10–50 over the broad temperature range 400–500 K. At the same time, the heat capacity has a singularity at $T \approx 450$ K (see Fig. 2.5 in Ref. 16). The lattice symmetry is not changed in the transition, but the lattice parameters are altered. $Ti_2O_3$ remains paramagnetic both above and below $T_c$.[110]

A diagram of the band structure of $Ti_2O_3$ has been proposed[111] and is presented in Fig. 7. According to this model, the Fermi level in the metallic phase intersects two d-bands that arise from the $t_{2g}$-level, which is split in the trigonal crystal field into $e_{\pi^-}$ and $a_1$-levels. As is proposed in Ref. 111, the change in the lattice parameters leads to a change in the band energy such that the $e_{\pi^-}$ and $a_1$-bands do not intersect. Since the $a_1$-band proves here to be completely filled, the state obtained is a semiconductor.

A self-consistent two-band theory of MDT's based on such a model of the spectrum has been constructed[112] with account taken of the Coulomb interactions (in the spirit of the Hubbard model—intraatomic ones) $U_{11}$, $U_{22}$ for each band and the interband interactions $U_{12}$. In the Hartree-Fock approximation these interactions lead simply to a shift of the bands, and since the matrix elements $U_{ab}$ differ, the shifts differ for each band.

The free energy calculated in Ref. 112 depends on three self-consistency parameters: the chemical potential $\mu$, the lattice distortion $R$, and the number of electrons in the $e_{\pi^-}$ band $n_2$. When $n_2 = 0$, the $e_{\pi^-}$ band is empty (semiconductor), while when $n_2 \neq 0$, this band is partially filled simultaneously with partial filling of band 1 (since $n_1 + n_2 = 1$)—this is a metallic state. Of course, the thermal scatter of the electrons has the result that $n_2 \neq 0$ at such temperatures, and hence the MDT proves to be smooth.

The theory enabled a qualitatively correct description

of the behavior of the lattice parameters, the heat capacity, and the magnetic susceptibility, as well as the effect of impurities on the MDT.

In closing this section we note the interesting properties of weakly doped $Ti_2O_3$: in the system $(Ti_{1-x}V_x)_2O_3$, even an addition of 0.5% V gives rise to metallic conduction and to the appearance of the properties of a spin glass. At larger $x$ the spin-glass state is replaced by antiferromagnetic order when the composition is closer to $V_2O_3 (x \gtrsim 40\%)$.[113]

### 3.5. The metal-dielectric transition in Magneli phases

A large number of oxides of vanadium and titanium with the general formula $Me_nO_{2n-1}$ ($n$ is an integer), called the Magneli phases, have MDT's. A detailed analysis of their complex crystal structure and physical properties is given in Ref. 5. Let us list the fundamental experimental data on which we can base a decision on the mechanism of the MDT.

1. In all the vanadium oxides with $3 \leqslant n \leqslant 9$ except $V_7O_{13}$, there are three temperature regions: a) paramagnetic metal, $T > T_c$; b) paramagnetic dielectric, $T_N < T < T_c$; c) antiferromagnetic dielectric, $T < T_N$.

2. The lattice symmetry does not change in the MDT. However, the cations are displaced from the centers of the oxygen octahedra, while the octahedra themselves are deformed.

3. In the metallic phase the ions $V^{3+}$ and $V^{4+}$ in $V_2^{3+}V_{n-2}^{4+}O_{2n-1}$ are disordered, but ordered in the dielectric phase.

4. The magnetic susceptibility above $T_c$ is intermediate in character between Curie-Weiss and Pauli behavior, and undergoes a break at the point $T_c$. The Neél temperature $T_N$ declines monotonically with increasing $n$.

In view of the low lattice symmetry of the cations and the large number of atoms in the cell, the band structure of the Magneli phases has not been calculated, and the number of theoretical studies on these compounds is small. These studies start with different models of the band structure of $V_2O_3$ or $VO_2$, which one can formally ascribe to Magneli phases with $n = 2$ and $n = \infty$, respectively.

An explanation of the MDT's involving the formation of CDW's has been proposed in Refs. 114 and 115 in different models of the electronic spectrum. Since formation of CDW's requires satisfaction of the nesting condition (3), one must explain its origin.

To understand the possible electron spectrum, let us calculate $\rho$—the number of electrons per cation. Each vanadium ion can yield five electrons to chemical bonding, of which two fill the p-shell of each of the $(2n - 1)$ oxygen ions. Consequently the number of band electrons is

$$\rho = \frac{5n - 2(2n-1)}{n} = 1 + \frac{2}{n}. \qquad (17)$$

Actually the models of Refs. 114 and 115 are distinguished by a differing distribution of the electrons over the bands. The model of Ref. 114 assumes that one electron per cation completely fills a certain lower band and plays no role, while the remaining $\delta\rho = 2/n$ electrons fill a singular band that satisfies the condition (3). When $n = 2$ this will be a half-

filled band. That is, the model of Ref. 114 starts with $V_2O_3$.

The Fermi level is lowered with increasing $n$, so that the fraction $1/n$ of the band is always occupied. Here the condition (3) is satisfied only for a one-dimensional band

$$\varepsilon(\mathbf{k}) = -W \cos ka. \qquad (18)$$

For three-dimensional bands it can hold only for half-filled bands. Peierls instability of the homogeneous state having the spectrum of (18) gives rise to formation of CDW's with an $n$-fold superstructure, which contradicts experiment on the invariance of the unit cell of $V_nO_{2n-1}$ in an MDT. Moreover, there are purely theoretical claims on the model of Ref. 114: a) when $n \to \infty$ the band of (18) will be empty, and thus the MDT in $VO_2$ cannot be described; b) it is difficult to imagine how the spectrum of (18), which is characteristic of a one-dimensional chain of cations, can be realized in a real $V_nO_{2n-1}$ structure; c) if it were realized in any way, then CDW's and SDW's cannot be formed in a one-dimensional chain.[116]

The model of Ref. 115, which starts with the spectrum of $VO_2$, seems more successful. For $VO_2$ a d-band with the condition (3) is known, and when $n = \infty$, only it figures in the treatment. Here we have $\rho = 1$, and the band is half-filled. With decreasing $n$ oxygen vacancies arise. In their field localized electron levels are formed with energies far below the Fermi level. It is assumed that the "extra" $\delta\rho = 2/n$ electrons fill these levels, and the band of (3) is half-filled as before, and splits into two subbands below $T_c$. The localized spins in the vacancy levels remain here in the paramagnetic state.

According to Ref. 115, the Coulomb interaction is the cause of the ordered arrangement of the vacancies along chains (one-dimensional order) and ordered arrangement of the chains (three-dimensional order).

Various mechanisms of antiferromagnetic ordering in $V_nO_{2n-1}$ are discussed in Ref. 115. Most of them involve the existence of a vacancy band $a_1$, which is formed by the overlap of the wave functions of the "extra" $\delta\rho$ electrons. This band must be rather narrow so as to fulfill the condition of Mott-Hubbard localization, which has been studied[117] in the case of a partially filled band.

As is known, interatomic hopping of electrons in a Mott-Hubbard dielectric leads to antiferromagnetism in the case of a half-filled band (see Sec. 5 of this review), but a tendency to ferromagnetism arises upon partial filling.[47] It can be exactly proved for $U \to \infty$ and with a single carrier in the case of simple cubic and bcc lattices that the ground state is ferromagnetic.[118] Hence the detailed microscopic theory must include the competition of mechanisms of ferro- and antiferromagnetic ordering. Since this has not yet been done, we must acknowledge that there is no microscopic understanding of the nature of the antiferromagnetism of Magneli phases.

A phenomenological theory of the MDT in Magneli phases based on the model of Ref. 115 has been constructed in the form of a two-parameter Landau expansion in terms of the singlet and triplet order parameters.[119] The result of this theory is the proof of the monotonic decline of $T_c$ and in-

crease of $T_N$ with decreasing $n$ from $VO_2$ to $V_2O_3$. However, actually $T_c$ varies nonmonotonically (see Ref. 5), which is explained in Ref. 119 by scattering by oxygen vacancies arranged in disordered fashion.[94]

The analysis of the experimental data performed in Ref. 123 leads to the conclusion that the correlation effects in the Magneli phases are stronger than in the extreme oxides of the series $VO_2$ and $V_2O_3$. However, owing to the nonintegral number of electrons, the system remains a metal with localized magnetic moments, which corresponds to the atomic limit of the Hubbard model (see Sec. 5). For this reason one must rather classify the Magneli systems among the systems with strong correlations, and the description of the MDT in them must be more complicated than the Hartree-Fock theory of CDW's or SDW's.

The dependence of the Neél temperature on the number $n$ has been derived from the semiphenomenological expression for the free energy of an antiferromagnetic semiconductor[114]

$$F(T) = -\frac{J}{2}(\delta\rho - n_2)^2 R^2$$
$$+ n_2 E_g - \frac{2T}{N} \ln \frac{(N/2)!}{(N_+)!(N_-)!(n_2 N/2)!}. \quad (19)$$

Here the first term is the energy of the ground state with the exchange integral $J$, $R$ is the relative magnetization of the sublattice, $n_2$ is the number of current excitations, the factor $\delta\rho - n_2$ reflects the fact that the magnetic moment per atom is $(\delta\rho - n_2) R$, the second term is the minimal energy of the current excitations through the gap $E_g$, and the third term is the entropy term. Expression (19) has been written previously for $\delta\rho = 1$ ($V_2O_3$) in Ref. 47 and is valid when $T \ll E_g$, when $n_2 \ll 1$ and one can neglect the distribution of excitations over the band, assuming that they all have the energy $E_g$. Since $T_N < T_c$, the condition $E_g \gg T$ is satisfied for all $T$ in the antiferromagnetic phase.

Upon minimizing (19) with respect to the parameters $n_2$ and $R$, we obtain the following self-consistency expressions:

$$n_2 = (\delta\rho - n_2)\exp\left(-\frac{E_g}{T}\right), \quad (20)$$

$$R = \text{th} \frac{JR(\delta\rho - n_2)^2 - U\exp(-E_g/T)}{T}. \quad (21)$$

Equation (21) without allowance for the current excitations (the last term in the argument of the hyperbolic tangent) reduces to the ordinary Curie-Weiss equation, which describes a second-order transition at the point $T_N^{(0)}$. However, here it leads to a first-order transition close to second order with $T_N < T_N^{(0)}$. Let us select the parameters entering into (20) and (21) such that $T_N$ for $n = 2$ coincides with the experimental value for $V_2O_3$.[66] Then let us assume that all the Magneli phases differ only in the concentration of electrons, and let us calculate $T_N(n)$. As we see from the table, the results agree well with the experimental data.

To explain the MDT's in the titanium oxides, one assumes electron-hole pairing from the "congruent" and vacancy bands.[115] However, there is no detailed theory. At the same time, the MDT in $Ti_4O_7$ possesses a singularity, namely: two conductivity jumps are known, and are separated by

TABLE I. Comparison of the experimental and theoretical values of the Neél temperature for Magneli phases.[114]

| $V_nO_{2n-1}$ | $\delta\rho$ | Experiment | Theory |
|---|---|---|---|
| $V_2O_3$ | 1 | 156 | 156 |
| $V_3O_5$ | 2/3 | 70 | 69 |
| $V_4O_7$ | 1/3 | 40 | 42 |
| $V_5O_9$ | 2/5 | 30 | 33 |
| $V_6O_{11}$ | 1/3 | 23 | 28 |
| $V_8O_{15}$ | 1/4 | 7 | 8 |

an interval of $\approx 20$ K. One of them is a semiconductor-semiconductor transition, while the other is a semiconductor-metal transition. For a discussion of the titanium oxides, see Ref. 5.

We note also the analogy between the MDT's in the Magneli phases and in magnetite $Fe_3O_4$, which was discussed in Ref. 5. Both cases are characterized by a disordered arrangement of the cations of different valency above $T_c$, and by their spatial ordering below $T_c$. It is not ruled out that one must combine the ideas of electron-hole pairing in an exciton dielectric with the ideas employed to describe transitions involving intermediate valency for a microscopic description of these substances.[13]

A large number of theoretical studies has been devoted to presenting polaron models of the MDT's in $Ti_4O_7$ and $Fe_3O_4$.[16,120] We note also the experimental study, Ref. 121 where an isotope shift of $T_c$ was found in magnetite upon replacing $^{16}O$ with $^{18}O$. This directly indicates the need to take account of the electron-phonon interaction in constructing the theory. An isotope effect has been found in the vanadium oxides $VO_2$, $V_3O_5$, and $V_2O_3$.[122]

Thus a theoretical treatment based on very simple models enables one to establish the causes of appearance of MDT's and to describe qualitatively the low-temperature thermodynamic properties of rather complicated compounds of the d (f) elements. Next comes the study of the kinetic characterisitcs and their singularities near MDT points. For this reason, Ref. 43 is of interest, in which the conductivity of a nonideal exciton dielectric at $T = 0$ is studied. An extremely essential point is that experiment indicates a defining role of the Coulomb and electron-phonon interactions, which are not at all small. Therefore calculations by the ordinary band theory of the Hartree-Fock type can only indicate correct trends, but not yield measurable values. Thus, in the compound NiS the experimental value of the dielectric gap is $\Delta_0 = 0.4$ eV with a band width $2W_1 = 1$ eV. According to (13), this corresponds to $\lambda_1 \sim 1$.

The problem of the possible construction of a perturbation-theory series in the reciprocal quantity $\lambda^{-1}$ and the finding of interpolation relations in the region of $\lambda \sim 1$ is discussed in Sec. 5 of this review.

## 4. FEATURES OF THE METAL-DIELECTRIC TRANSITION IN MATERIALS WITH LOCALIZED MAGNETIC MOMENTS

As a rule, in the rare-earth metals and their compounds, the electrons are well separated into localized f-electrons,

which form a localized magnetic moment (LMM), and collectivized s-, p-, and d-electrons; the s–d (f) exchange model can be applied to describe such substances.[35] Such a sharp division usually does not exist in compounds of the 3d-metals, but in the series of compounds of Cr, Mn, and Fe— elements from the middle of the row, where the tendency to localization is greatest—LMM's can exist, at least in the zero-order approximation with respect to hybridization and other perturbations that mix the band and atomic states.[124] Apparently, this is the situation in FeS and CrS, whose MDT's are discussed in the reviews of Refs. 32, 125. Let us present the fundamental properties of these substances.

One observes the following sequence of phase transitions in FeS with decreasing $T$: a paramagnetic metal-antiferromagnetic metal transition ($T_N = 600$ K), an easy plane-easy axis magnetic orientational transition ($T_s = 445$ K), and an antiferromagnetic metal-antiferromagnetic dielectric transition with doubling of the period along the hexagonal axis ($T_c = 420$ K).

The sequence of transitions in CrS upon cooling differs: a paramagnetic metal-paramagnetic dielectric transition with doubling of the period along the $c$-axis ($T_c = 600$ K), and a paramagnetic dielectric-antiferromagnetic dielectric transition ($T_N = 450$ K).

X-ray photoemission data[126] have shown that the hybridization of the 3d-states of sulfur in FeS is weaker than in NiS. Whereas in NiS the 3d-band is superposed on the upper part of the 3p-band, in FeS the 3d-bands lie above the 3p-bands. A possible scheme of the energy structure of FeS below and above $T_c$ is presented in Ref. 127. In this model the metallic properties are associated with the half-filled $d_{z^2}$-band, which is formed by overlap of the cationic $e_g$-orbitals $d_{z^2}$. As is assumed, the remaining $d^5$-electrons form the term $^6A_1$ with the spin $S = 5/2$. Below $T_c$ the $d_{z^2}$-band is split into two subbands, the lower of which is completely full at $T = 0$, while the upper is empty. Within the framework of perturbation theory, the description of the MDT in this model cannot be restricted only to interactions of the band electrons, but must allow also for interaction with the localized spins.

In this regard a number of studies have constructed a theory of MDT's in an s–d model in which the conduction band satisfies the nesting condition (3). In the latter, in addition to the singlet and triplet intraband pairings, an instability of the paramagnetic system of the LMM's can arise from the s-d exchange interaction and the formation of density waves of the LMM's.[128] Under nesting conditions it is insufficient to restrict the treatment to second-order perturbation theory in the s–d exchange $J$ for calculating the indirect interaction between the LMM's, but one must sum all the electron-hole loops with the transferred momentum $\mathbf{Q}$. In essence this is the same instability as has been used[129] to explain the possible magnetic structures of the rare-earth metals.

For a self-consistent description of the dielectric phase in this case one must introduce three order parameters—the gaps $\Delta_s$ and $\Delta_t$ and the amplitude of the density wave of the LMM's $\langle S_f^z \rangle = \langle S^z \rangle \exp(i\mathbf{Q}f)$. This problem has been solved for a ferromagnetic[130] ordering of the LMM's and for an antiferromagnetic[101,131] ordering. Reference 101 also treated the more general case in which two bands exist—one with the spectrum of (3) and the other nonsingular.

We note that the effects of the exchange interaction of LMM's and band electrons in the case of a Fermi surface with nesting differ from the case of ordinary electrons. While usually the carriers in the broad-band s–d model ($J \ll 2W$) serve only to establish the indirect exchange interaction, and we can neglect their magnetization and Coulomb correlations, the situation differs in the nesting case. An arbitrarily small intraband interaction leads to formation of SDW's; if the LMM's do not interact with one another in any way, then the paramagnetic system of the LMM's lies in an inhomogeneous molecular field and is magnetized in it, so that at $T = 0$ we have $\langle S^z \rangle = S$ sgn $J$. The sign of $J$ affects the mutual orientation of the LMM's and the band moment; they can exist in phase or counterphase. Here the triplet gap in the spectrum of the electrons increases and consists of two contributions—from the band and from the LMM's. This implies that $T_c$ also increases.[130,131]

The situation is more interesting in which one takes account of the spin-phonon interaction caused by magnetostriction. The linear coupling between the deformations and the magnetic structure prevents one from separating the SDW's from the CDW's. Therefore singlet and triplet orderings coexist even when $\rho = 1$, whereas this was impossible in the band theory.[37] These conclusions are corroborated both by the analytic solutions of the self-consistency equations at $T = 0$ and by numerical study of them at finite $T$.[131]

The theory of MDT's in the s–d model presented here qualitatively reflects certain features of the MDT's in CrS and FeS: the $T_c$'s in substances having LMM's are usually higher ($\sim 10^3$) than in band systems ($\sim 10^2$); the coexistence of antiferromagnetism and lattice distortion is characteristic of the ground states of FeS and CrS. Nevertheless, the sequence of phase transitions indicated at the beginning of this section is not described by the theory. Moreover, the electronic structure of FeS and CrS must be treated in more complex multielectron models. One of the variants of these models has been proposed.[32] However, there is currently no detailed study of MDT's in the multielectron theory.

## 5. METAL-DIELECTRIC PHASE TRANSITION IN SYSTEMS WITH STRONG INTRAATOMIC CORRELATIONS

At present a broad class of compounds is known with an unfilled electron shell, called the Mott insulators, which are dielectrics at normal pressures, but which transform with increasing temperature to a completely disordered state with no substantial change in the dielectric gap (see the review by Wilson[132]). As an example, let us examine the phase diagram of vanadium sesquioxide $V_2O_3$, which has been obtained in a series of studies by McWhan et al.,[133–135] and is presented in Fig. 8. Upon passing through the line $L$, a second-order phase transition occurs with disappearance of the antiferromagnetic order parameter, but without disappearance of the dielectric gap. On passing through the line $K$ (with decreasing pressure), a dielectric gap appears practi-
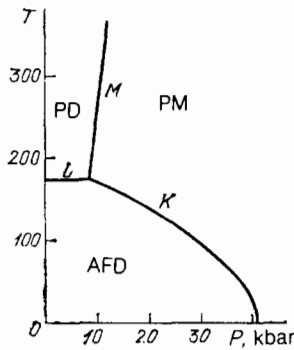
FIG. 8. Phase diagram of the solid solution $(V_{1-x}Cr_x)_2O_3$ for $x = 0.0375$.[134]

cally simultaneously with the antiferromagnetic order parameter, so that we can interpret this transition as the formation of an SDW. On passing through the line $M$ a sharp change in conductivity occurs, but the form of crystal structure does not change: in both phases the unit cell has the corundum structure, which persists in the disordered paramagnetic phase. Wilson and Pitt[136] observed a qualitatively similar situation in the compound $NiS_2$. Here passage through the line $M$ is accompanied by a small change in the volume of the unit cell, which has a pyrite-type structure in both high-temperature phases, remaining paramagnetic when $T > T_N$ (Fig. 9). One can understand intuitively that the source of the dielectric gap is the strong intraatomic electron-electron correlations, as is confirmed by the Hubbard theory. The physics of the transition from the parametallic to the paradielectric state (through the $M$-line) is considerably less well understood. The fundamental theoretical problem here consists in finding an order parameter that disappears or arises in passing through the line of disappearance of the dielectric gap.

### 5.1. The Hubbard theory and the metallic order parameter

In his study[24] Hubbard starts with the atomic limit, where one can neglect the overlap of the electronic wave functions—the zero-order approximation. In the next approximation one can take account of the collectivization of the atomic states owing to one-electron intercell transitions.
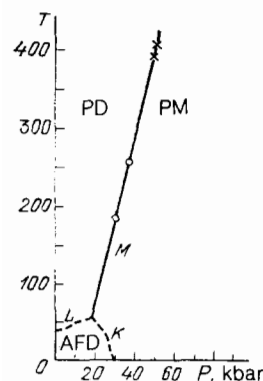


FIG. 9. Phase diagram of the compound $NiS_2$.[136]

The so-called Hubbard I solution, which pertains to the paraphase, but without taking account of scattering by the fluctuations of the local spin, was derived in this way. Thus, for the very interesting case in which the number of electrons equals the number of cells, Hubbard obtained two allowed bands[24]:

$$\varepsilon^{\pm}(\mathbf{k}) = \frac{1}{2}\left[t(\mathbf{k}) \pm (t^2(\mathbf{k}) + U^2)^{1/2}\right].\tag{22}$$

Generalization of the Hubbard theory to the case of an antiferromagnetic material with two identical sublattices also yields two allowed bands:

$$\varepsilon^{\pm}(\mathbf{k}) = \pm\left(t^2(\mathbf{k}) + \frac{U^2}{4}\right)^{1/2}.\tag{23}$$

The notation is the same as in Sec. 2 [see Eqs. (1) and (2)]. Even in this very simple approximation Hubbard found a result that the band theory cannot yield—a dielectric gap exists in both the antiferromagnetic and paramagnetic phases. Its maximum value ($U$) is attained in the atomic limit. However, according to (22) and (23) it exists also in the band limit—with an arbitrarily small value of the Hubbard energy $U$. This result is the major defect of the Hubbard I solution, since when $U \to 0$, the system must possess the metallic properties of a weakly nonideal Fermi gas.

In one of the following studies[137] (below—Hubbard III), Hubbard takes account of the scattering of electrons by the static fluctuations of the local spins. Here he obtained not only a transition from the dielectric to the metallic state, but also found a highly important property of a Hubbard dielectric—the magnetic susceptibility has a characteristic temperature-dependence of the Curie-Weiss type throughout the region of existence of the paraphase. The existence of this dependence, which arises from the presence of local moments, in the vicinity of the metal-dielectric transition and also in the metallic phase, has extremely expanded the region of applicability of the Hubbard model, not only toward compounds of the transition elements but also to the transition metals themselves and the rare-earth metals, in which one always observes a Curie-Weiss law.

It was necessary to understand how the transition occurs to the band limit, where local moments are absent. This question has been answered within the framework of the Hubbard model by Syrot.[138,139] He showed by using the method of functional integration that one can find two singular points from the side of the band limit: a) where a local moment and a nonzero value of the Curie-Weiss constant arise; and then b) where a transition to a dielectric paramagnetic phase occurs.

In the theory of Ref. 139 which corresponds to the self-consistent-field approximation, the condition for existence of local magnetic moments (LMM's) has the form of the Stoner criterion averaged over the random and independent arrangement of the spins

$$\overline{U\rho(E)} = \frac{U}{\pi}\operatorname{Im}\int[F^{(0)}(E)]^2 n(E)\,dE > 1.\tag{24}$$

Here we have

$$F^{(0)}(E) = \sum_{\mathbf{k}}\frac{1}{E - t(\mathbf{k}) + i\delta} = \int\frac{\rho_0(\varepsilon)\,d\varepsilon}{E - \varepsilon + i\delta};$$

$n(E)$ is the Fermi distribution, and in the limit as $T \to 0$ we have $n(E) = \theta(-E)$. Here and below, $\delta$ is a small positive increment,

$$\theta(x) = \begin{cases} 1 & \text{for } x > 0, \\ 0 & \text{for } x < 0, \end{cases}$$

and $\rho_0(\varepsilon)$ is the start-up density of one-particle states.

The transition from the dielectric to the metallic state occurs even in the region of existence of LMM's of (24), mainly because of the scattering of the electronic excitations by fluctuations of the LMM's.

The properties of the Hubbard model in the region of small $U$, where LMM's are absent, have been studied by Gutzwiller.[140] Upon using a suitable test function in the region

$$U < C_0 = -16 \sum_{\mathbf{k}} t(\mathbf{k}) n[t(\mathbf{k})], \tag{25}$$

he was able to determine the number of pairs $(d)$ localized at a single node, and also to prove that the jump in the distribution of single-particle excitations $(q)$ vanishes precisely at $U = C_0$:

$$d = \frac{1}{4}\left(1 - \frac{U}{C_0}\right), \qquad q = 1 - \frac{U^2}{C_0^2} = \frac{m}{m^*}. \tag{26}$$

The latter relationship for the effective mass $m^*$ was derived by Brinkman and Rice[55] on the basis of the Landau theory of the Fermi liquid (see Ref. 142).

A numerical analysis of the relationships (24) and (25) shows that formally these inequalities do not contradict one another. In other words, at the point where LMM's appear, beyond which the Gutzwiller theory ceases to hold, all three quantities $d$, $q$, and $m^*$ remain finite. Thus, in the model of a semielliptical (SE) band, for which

$$\rho_0(\varepsilon) = \frac{2}{\pi W^2}(W^2 - \varepsilon^2)^{1/2}, \tag{27}$$

the condition for appearance of LMM's has the form $U = (3\pi/8)W$; the transition point to the dielectric state is determined by the quantity $U = U_c = (4/3)W$, and the Brinkman-Rice point $U = C_0$, where the effective mass becomes infinite, arises at the even greater values[3] $U = C_0 = (32/3\pi)W$. Numerical integration of relationships (24) and (25) for a simple cubic lattice yields the value $U \leqslant 0.82\ W$ for the point of appearance of LMM's,[150] and $U = 2.56\ W$ for the Brinkman-Weiss point.[141]

The Hubbard III theory starts with the atomic limit where LMM's always exist, so that its results are qualitatively valid throughout the region of (24), and in particular, in the neighborhood of the metal-dielectric transition.

In the Hubbard theory it is convenient to introduce the new quantity $\tilde{\omega}$ instead of the Green's function of virtual electrons calculated in his study, summed over all momenta $(F)$:

$$\tilde{\omega} = \frac{i(U^2 + 4\omega^2)}{FW^2}.$$

With this definition the function $\tilde{\omega}$ for $|\omega| \ll U$ is proportional to the density of states $\rho(\varepsilon)$ for the given energy $\varepsilon = i\omega$, as referred to the Fermi level. This function essentially deter-

mines the properties of the system at the Fermi level: in the metallic phase it is finite, and decreases as we approach the transition point; in the dielectric phase we have $\tilde{\omega}(0) = 0$, which corresponds to the forbidden band, which owes its existence to the correlation gap.

According to the Hubbard theory,[137] in the SE band model of (27), the function $\tilde{\omega}$ satisfies a cubic equation with coefficients that depend as power functions on $\omega$. Just like the function $F$, the quantity $\tilde{\omega}$ is an odd function of the complex frequency $\omega$. However, in contrast to $F$, in the dielectric phase it vanishes as $\omega \to 0$. If the energy $i\omega$ is small in comparison with $U$, then the equation for $\tilde{\omega}$ reduces to the canonical form:

$$\tau\tilde{\omega} + b\tilde{\omega}^3 = \omega. \tag{28}$$

Here we have $b \sim U^{-2} > 0$, while the dimensionless parameter $\tau$ is small and determines the closeness of the system to the metal-dielectric transition point [see Eqs. (31) and (33) below].

The region $\tau < 0$ corresponds to the metallic phase having a finite density of states at the Fermi level

$$\rho(0) \sim \tilde{\omega}(0^+) = \left(-\frac{\tau}{b}\right)^{1/2}. \tag{29}$$

When $\tau > 0$, a nonzero density of states arises for a finite value of the energy $i\omega$, which corresponds to the dielectric gap

$$E_g = \frac{2}{b^{1/2}}\left(\frac{\tau}{3}\right)^{3/2}. \tag{30}$$

Equation (28) is very general: any self-consistent process describing the process of closing of the gap without the vanishing of any thermodynamic order parameter leads to Eq. (28) near the point where the gap vanishes. We can present the theory of superconductors with paramagnetic impurities as the historically first example,[95] and then the theory of a nonideal exciton dielectric.[94] In the Hubbard model the coefficients $\tau$ and $b$ have been calculated by Zaĭtsev[27]:

$$\tau = 1 - 4\gamma \sum_{\mathbf{k}} t^2(\mathbf{k}) U^{-2},$$
$$b = 64\gamma U^{-6}[\sum_{\mathbf{k}} t^4(\mathbf{k}) - (\sum_{\mathbf{k}} t^2(\mathbf{k}))^2]. \tag{31}$$

According to Ref. 143, the coefficient $\gamma$ is proportional to the product of the temperature and the magnetic susceptibility. In the atomic limit we have $\gamma = 3$, and Eq. (31) completely agrees with the Hubbard III theory (with $|\omega| \ll U$ and $|\tau| \ll 1$).

All the thermodynamic quantities can be expressed in terms of the summation over the frequencies of functionals that depend on $\tilde{\omega}$ and $\omega$. Here the singularities near the Mott-Hubbard transition point (termed below the M-H transition) are defined in terms of Eq. (28). Thus one can find in the limit as $T \to 0$ the singular component of the total energy of the system $(E_{an})$. According to Ref. 154 we have

$$E_{an} \sim -(-\tau)^{7/2}\,\theta(-\tau). \tag{32}$$

The number of pairs $(d)$ per cell does not vanish for any value of the ratio $U/W$. However, one can show that near the

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MDT this function has a singular component ($d_{an}$), which is calculated by the same method as the anomalous component of the energy:

$$d_{an} \propto -(-\tau)^{3/2}\,\theta\,(-\tau).$$

Thus, in the region of existence of local moments (where $\gamma \neq 0$, and the relationships (26) are invalid), the quantity $\tilde{\omega}$ is the sole function that vanishes near the metal-dielectric transition point similarly to the order parameter in the theory of second-order phase transitions.[144] For this reason we shall call it the metallic order parameter below. The complex frequency $\omega$ acts as the conjugate quantity, while the quantity $\tilde{\omega}$ itself is proportional to the density of states at the Fermi level in the limit as $\omega \to 0$ [see Eq. (29)].

In the far-lying metallic phase in the presence of strong elastic scattering of electrons by impurities, an analogous quantity was introduced by Wegner.[145] He wrote [146] " . . . . The system has an internal isotropic symmetry with the frequency as the source and the density of states as the order parameter." It has been shown in the theory of localization[147] that mainly the transverse components of the multicomponent order parameter fluctuate at the localization point, similarly to the fluctuation of the transverse components of the spontaneous moment in a two-dimensional ferromagnet near the temperature of absolute zero.

Near the Mott-Hubbard transition point, where an equation of the Ginzburg-Landau type (28) holds in the self-consistent-field theory, both the transverse and the longitudinal components of the metallic order parameter fluctuate strongly.[43] This idea is the basis of the correlation theory of the metal-dielectric transition.

### 5.2. Phase transition in the paramagnetic phase

There is an extensive literature that refines and develops the Hubbard theory. The most modern approach, which is based on the method of functional integration,[148,149] was proposed by Cyrot[139] and by Moria and Hasegawa.[150] Despite the fact that these studies do not take account of the transverse fluctuations of the spins, the longitudinal fluctuations, which are characterized by the quantity $\langle \zeta^2 \rangle$, are calculated in self-consistent fashion at the Mott-Hubbard transition point itself. Upon introducing the complex frequency $i\omega$ instead of the energy $\varepsilon$, and the metallic order parameter $\tilde{\omega} = iW^2/4$ instead of the intrinsic-energy component $\Sigma(\varepsilon)$, we again obtain Eq. (28) near the transition point and as $\omega \to 0$, with the coefficients

$$\tau = \frac{U\langle \zeta^2 \rangle}{W^2} - 1, \quad b = \frac{4}{W^2}. \tag{33}$$

A numerical integration of the self-consistency equations at the transition point itself has been given in Ref. 138, where the value $\langle \zeta^2 \rangle^{1/2} = 0.74$ was obtained. Mertsching[151] and Hasegawa[152] give close-lying numerical values. However, the following temperature corrections were obtained in Ref. 151:

$$\left(\frac{U}{W}\right)_c = \frac{4}{3} + \frac{8T}{3W} + 4{,}418 \left(\frac{T}{W}\right)^{5/3}. \tag{34}$$

As we see from Figs. 8 and 9, the M-H transition line in

the variables $(T, P)$ actually has a small temperature slope. However, the dependence (34) proves too weak. Upon differentiating the condition for an M-H transition with respect to the temperature, we can show that the slope of the transition line in a cubic crystal is determined by the product of the thermal-expansion coefficient ($\alpha$) by the hydrostatic compression modulus ($K$). For $V_2O_3$ this relationship yields a result elevated above the experimental value by a factor of 4.5. This difference can be ascribed to electron-phonon interaction, which effectively weakens the interaction $U$. At a temperature above the Debye temperature, at which the one-phonon contribution is proportional to the first power of the temperature, we have[153]

$$\frac{dP_c}{dT} = K\left(\alpha + \frac{\psi\gamma^{1/2}}{z^{1/2}}\frac{\partial \ln \theta}{\partial t}\right). \tag{35}$$

Here $\vartheta$ is the volume of the unit cell, $t$ is the overlap integral expressed in the same units as the coefficient of thermal expansion $\alpha$, and $z$ is the number of nearest neighbors. According to Ref. 153, the coefficient $\psi$ is expressed in terms of the ratio of the static electron-phonon interaction constant to the square of the Hubbard energy $U$. The coefficient $\psi$ is small, but its contribution is of the same order of magnitude as the thermal-expansion coefficient.

As we have already noted, the Hubbard model *per se* yields a very weak singularity of the energy of the system near the transition point. According to Refs. 154 and 155, as $T \to 0$, we have a singularity that corresponds to a phase transition of order 3.5 [see also (32)]. The experimental study of the Mott transition in transition-metal compounds shows that it is accompanied by a weak isostructural first-order transition (see Fig. 10, which is taken from Ref. 156, and the experiments[157] in which two-phase regions were found in the system $(V_{1-x}Ti_x)_2O_3$). To eliminate this contradiction, Mott proposed[158] that the free energy as a function of the volume must have two minima. If one takes account of the well-known general Peierls-Landau-Zel'dovich concepts, one can easily understand[159] that the origin of the second minimum is explained by the sharp change in the long-range component of the Coulomb interaction. Ultimately the latter involves the onset of exponential screening upon transformation from the dielectric to the metallic phase. Upon extrapolating from the low-temperature region, we note that the reciprocal square of the Debye screening radius $R$ is proportional to the density of states at the Fermi level. Hence, by using Eq. (29) we obtain
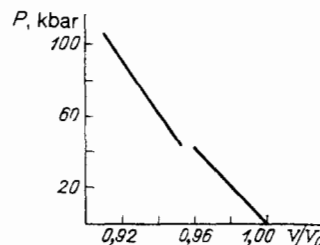
$$R \sim (-\tau)^{-1/4}\,\theta\,(-\tau).$$

FIG. 10. Experimental critical isotherm ($T = 293$ K) of pure $NiS_2$.[156]

Using the Debye-Huckel theory (which corresponds to the perturbation theory in the long-range component of the Coulomb interaction), we directly find the singular contribution to the polarization component of the free energy[159]:

$$\Delta F \sim -R^3 \sim (-\tau)^{3/4} \theta(-\tau). \qquad (36)$$

In the general case we have

$$\Delta F \sim -(-\tau)^{\beta'} \theta(-\tau). \qquad (37)$$

Here the perturbation theory has $\beta' = 3/4$; the correlation theory[43] of the $\varepsilon$-expansion type yields a stronger power-function singularity, $\beta' = 11/12$.

Thus, in agreement with the Mott hypothesis, the free energy at $T = 0$ and $\tau \to 0$ has a 90-degree "cusp," which becomes diffuse with increasing temperature. Upon expanding the enthalpy in powers of the deformation with allowance for the singular component of (37), one can derive a very simple relationship between the hydrostatic compression moduli in the metallic ($K_m$) and dielectric ($K_d$) phases pertaining to the first-order transition point[160]:

$$K_m - K_d = \frac{2K_d(1-\beta')}{\beta'} . \qquad (38)$$

Here $\beta'$ is the exponent in the singular component of the expansion in the enthalpy as $T \to 0$. Substitution into (38) of the values of $K_m$ and $K_d$ for $NiS_2$ yields $\beta' = 0.87$, lying just between the values yielded by the self-consistent-field theory (36) ($\beta' = 0.75$) and the correlation theory of the $\varepsilon$-expansion type ($\beta' = 11/12 \approx 0.92$).

### 5.3. Phase transition in a magnetically ordered phase

With decreasing temperature, a Hubbard-type system becomes ordered. According to Slater,[17] in alternant-type lattices (bcc, simple cubic), antiferromagnetic ordering sets in at an arbitrarily small value of the energy $U$. In nonalternant lattices (of the type of fcc or hcp), a critical value of the ratio of the Hubbard $U$ to the width $W$ of the conduction band always exists, above which antiferromagnetic ordering

arises in the system. According to Ref. 151, the critical ratio for a fcc lattice is $(U/W)_c = 0.72$.

Mertsching[151] has calculated the Neél temperature for arbitrary values of $U$ and for the special case of an SE band (Fig. 11). Here it turned out that the Neél temperature in the variables $T/W$ and $U/M$ has a maximum near the critical value corresponding to the metal-dielectric transition point in the paraphase. One can obtain an analogous curve for any alternant lattice if one finds the point of antiferromagnetic instability in the paraphase under the condition of complete nesting (3).[27,161] Here, according to Ref. 150, for a simple cubic lattice, and also in the model of an SE band, the maximum value of the Neél temperature proved to be two orders of magnitude smaller than the Hubbard energy (as we see from Fig. 11).

Upon studying the experimental situation depicted in Figs. 8 and 9, one might conclude that the M-H transition line breaks off at the magnetic-ordering line. However, no physical justification exists for this. The reason for the disappearance of the dielectric gap in the Hubbard III model is the scattering of electrons by fluctuations in the localized spins. In passing through the magnetic-ordering line, the spin fluctuations are weakened but do not vanish.[161] Here, according to Ref. 162, near the transition point the correction to the coefficient $\gamma$ in Eq. (31) is decreased in proportion to the square of the antiferromagnetic order parameter.

$$\gamma \approx 3 - 5 \frac{T_N - T}{T_N} \theta(T_N - T). \qquad (39)$$

Substitution of this expression into (31) enables one to estimate the region of existence of the antiferrometallic phase for a given deviation of the pressure from the critical point ($\Delta P$):

$$\frac{T_N - T_{M-H}}{T_N} = -\frac{6\Delta P}{5K} \frac{\partial(\ln W)}{\partial(\ln \vartheta)} . \qquad (40)$$

For transition-metal compounds the derivative $\partial \ln W / \partial \ln \vartheta$ does not exceed three, so that we obtain a small value not exceeding several percent for characteristic values of the
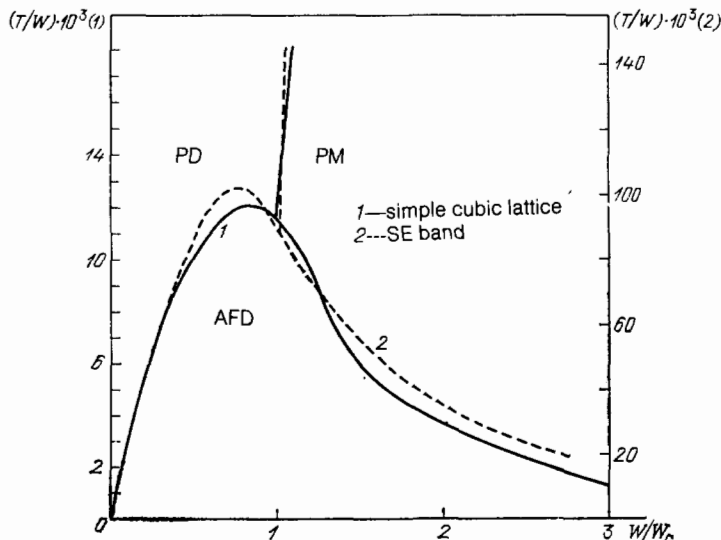


FIG. 11. Theoretical phase diagram of the Hubbard model in the case of a simple cubic lattice obtained by Moria and Hasegawa[150] (1) and for the semielliptic distribution of (27) from Refs. 151 and 152 (2).
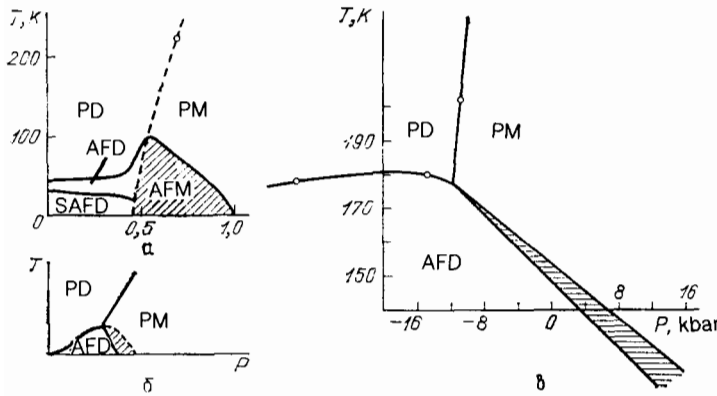
FIG. 12. a—Experimental phase diagram of the solid solution Ni(S, Se)$_2$, where an antiferrometallic phase (cross-hatched) was first discovered.[165] b—Hypothetical phase diagram of the Hubbard model with strong breakdown of the nesting condition.[139] c—Proposed region of existence of an antiferrometallic phase in the neighborhood of a tetracritical point of the compound V$_2$O$_3$ and solid solutions based on it; the M-H transition line in the antiferromagnetic phase was obtained by using Eq. (40).

hydrostatic compression modulus of 1–2 mbar and $P \sim 10$ kbar. The relationships (39) and (40) are applicable to any lattices, regardless of the exactness of fulfillment of the nesting condition (3). For this reason we must assume that in all cases the M-H transition line deviates sharply toward higher pressures after intersecting the magnetic-ordering line.[4]

For a theoretical analysis of the possible existence of an antiferromagnetic phase with complete nesting and in the model of an SE band in the Hasegawa equations,[152] let us transform to the variables

$$8i\widetilde{\omega} = W^2 (\Sigma_+^{-1} + \Sigma_-^{-1}), \quad 8\widetilde{\Delta} = W^2 (\Sigma_+^{-1} - \Sigma_-^{-1}). \quad (41)$$

The quantity $\widetilde{\omega}$ has the meaning of the metallic order parameter, while $\widetilde{\Delta}$ is proportional to the mean moment of one of the sublattices. If we assume the possible existence of a gap-free phase ($\widetilde{\omega} \neq 0$ with $\omega = 0$) and then take the limit with $\widetilde{\omega}^2 \ll \widetilde{\Delta}^2$, we obtain the equation of the Mott-Hubbard transition line in the antiferromagnetic phase:

$$2U_c^2 \langle \zeta^2 \rangle = [1 + (1 - \alpha^2)^{1/2}] W^2, \quad \alpha = \frac{(\langle \zeta \rangle)^2}{\langle \zeta^2 \rangle} . \quad (42)$$

Here $\langle \zeta \rangle$ and $\langle \zeta^2 \rangle$ are the mean and mean-square values of the local moment. When $\langle \zeta \rangle = 0$ we obtain a result pertaining to the paraphase [see (33), with the condition $\tau = 0$].

Moving into the ordered phase corresponds to an increase in the parameter $\alpha$. Here the critical value $W_c$ of the width of the electron band at the boundary with the antiferromagnetic phase also increases. Thus, near the point of intersection of the lines of the second-order transition and the metal-dielectric transition, where $W = W_c^*$, we have

$$W_c = W_c^* \left( 1 + \frac{\alpha^2}{8} \right). \quad (43)$$

The rms fluctuations of the spontaneous moment rapidly decrease with decreasing temperature, and vanish as $T \to 0$.[152] Here $\alpha = 1$, while in the model of an SE band, according to (12), we have

$$\langle \zeta \rangle \sim \exp \left( -\frac{\pi W}{2U} \right). \quad (44)$$

Thus, when $U \ll W$, the condition (42) cannot be fulfilled. Hence we conclude that an antiferromagnetic phase under conditions of complete nesting can exist only at a finite temperature below $T_N$ (see Fig. 12c).

In nonalternant lattices the rms fluctuations of the local moment differ from zero at all temperatures. For this reason, in the given case an antiferromagnetic phase exists also at $T = 0$ (see Fig. 12a). According to Ref. 139, in an fcc lattice a type-I antiferromagnetic phase at $T = 0$ exists in the interval $0.89U < W < 1.39U$. In real alternant lattices, where the nesting condition (3) is satisfied only approximately, antiferromagnetic order exists also at $T = 0$, but to the extent that transitions to the second nearest neighbors exist (see Fig. 12b, Eq. (4), and also Ref. 163).

Near the M-H transition line, the metallic order parameter satisfies the Landau equation (28) with coefficients depending on the magnitude of the antiferromagnetic order parameter. In nonalternant lattices or in the case of incomplete nesting, the equation for $\widetilde{\omega}$ contains a term quadratic in $\widetilde{\omega}$, but with a purely imaginary coefficient. Here we must recall that the frequency $i\omega$ always enters in combination with the chemical potential, which is a consequence of Galilean invariance[18]:

$$\tau \widetilde{\omega} + i\alpha \widetilde{\omega}^2 + \beta \widetilde{\omega}^3 = \omega - i\mu. \quad (45)$$

Upon using the obvious transformations $\widetilde{\omega} \to \omega - i(\alpha/3\beta)$, we have

$$\mu \to \tau \frac{\alpha}{3\beta} + \frac{2\alpha^3}{27\beta^2} .$$

Again this equation reduces to the canonical form (28), but with a shifted transition point $\tau \to \tau + (\alpha^2/3\beta)$.

In nonideal crystals of the type of the solid solution Ni(S$_{1-x}$Se$_x$)$_2$ or V$_{2(1-x)}^{3+}$V$_{2x}^{4+}$O$_{3-x}$, a sharp decrease in the Neél temperature occurs with increasing concentration, simultaneously with expansion of the region of existence of the metallic phase (see Figs. 12a and 13). The reason for this lies in an additional mechanism of scattering by composition fluctuations, which is equivalent to a concentration increase in the parameter that enters into (31). In the general case, if one allows for the fluctuations of the hopping integrals (nondiagonal disorder) as well as the fluctuations of the electrostatic potential (diagonal disorder), Eq. (28) will be valid as before near the M-H transition point, but with coefficients that depend on the concentration.[162,164] With decreasing temperature, the nonthermodynamic composition fluctuations persist even at the absolute zero of temperature. For this reason one can observe an antiferromagnetic phase even
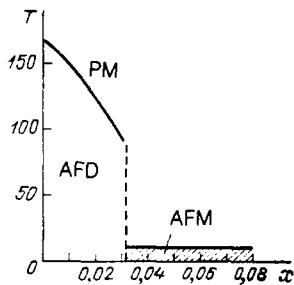
FIG. 13. Phase diagram of the solid solution $(V_{1-x}^{3+}V_x^{4+})_2O_{3+x}^{2-}$.[166]

at $T = 0$, but at not too small a concentration $x$, as we see from Figs. 12a and 13.

## 6. CONCLUSION

In this review we have tried to offer a view of the physical picture of the phase transition from the metallic to the dielectric state in compounds of the transition metals, where electron-electron interactions are essential. Systems with weak correlation have been treated within the framework of models of overlapping bands. In nonideal systems and in systems with strong correlation it is extremely convenient to use the concept of the metallic order parameter to describe the transition. By using it one can describe the singularities of the physical parameters and the processes that occur near the transition point. As we see it, the further development of the theory of the metal-dielectric transition must lie in the direction of greater concretization of the electronic structure, which rests on band calculations of the self-consistent-field type with account taken of the existence of the metallic order parameter and detailed accounting taken of the Coulomb and exchange correlations in the presence of a possible onset of anomalous means corresponding to charge, spin, and orbital ordering.

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[1]It is important to recall the study of S. P. Shubin and S. V. Vonsovskiĭ,[2] in which an attempt was first made to refine the criterion of the metallic state with allowance for strong electron-electron correlations.

[2]Actually band 1 ($e_g$) is twofold degenerate in the crystallographic index. One must take this into account in calculating both the magnetic susceptibility and all the other thermodynamic quantities.

[3]It was shown[141] that the choice of an improved two-parameter test function, but as before without taking account of LMM's, leads to the conclusion that no singularity is present at $U = C_0$.

[4]We should note that, in trying to find agreement with the experiment Moria and Hasegawa,[150,152] conclude that an antiferrometallic phase cannot exist at $T < T_N$ (see Fig. 11). This statement is based on numerical integration. However, the discussions below prove the existence of a narrow region of existence of an antiferrometallic phase.

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