Metal–insulator transition: the Mott criterion and coherence length

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Abstract
On the basis of the Mott criterion for metal–insulator transition (MIT), an
expression for the correlation length, identical to that for the coherence
length in the theory of superconductivity, is obtained. This correlation length
characterizes the size of an electron–hole pair (in an excitonic insulator) or the
effective Bohr radius (as, e.g., in doped semiconductors). The relation obtained
is used for calculation of the coherence length in vanadium dioxide. The
presence of two characteristic coherence lengths ($\xi_1 \sim 20$ Å and $\xi_2 \sim 2$ Å) is
found. This is associated with the specific features of the transition mechanism
in VO_2: this mechanism represents a combination of the purely electronic
Mott–Hubbard contribution and the structural (Peierls-like) one. It is shown,
however, that the driving force of the MIT in VO_2 is the electron-correlation
Mott–Hubbard transition.

1. Introduction

Metal–insulator transition (MIT) is one of the most vital and spectacular problems in condensed
matter physics. Recently this problem has received renewed attention, primarily due to the
discoveries of high-T_c superconductivity and colossal magnetoresistance in perovskite-like
metal oxide cuprates and manganites [1].

   The Mott criterion plays a special role in this problem. It states [2] that

$$a_H n_c^{1/3} \approx 0.25, \tag{1}$$

where a_H is the effective Bohr radius and n_c is the critical carrier density at the transition. This
simple criterion provides a numerical prediction for the MIT in many different systems [3]—
from doped semiconductors and high-T_c superconductors (HTSC) to metal–ammonia solutions
and metal–noble gas alloys. That is why the problem of the criterion (1)—both experimental
measurements of n_c, and more precise theoretical calculations of the constant in the right-hand
side—has received much attention in the literature; there are a huge number of works devoted
to this topic (see, e.g., [4] and references therein).

However, the generally known example of the MIT in doped semiconductors (with an increase in the impurity concentration) is far from being the only one. There are a lot of materials (mainly compounds of transition and rare-earth metals) exhibiting a temperature-induced MIT [1–3], likewise other usual phase transitions—superconducting, ferroelectric, or magnetic. For transition metal compounds, there is no consistent and unified theory of MIT, unlike the case for doped semiconductors, for which all is more or less clear, at least conceptually [1–4]. Instead, there are a variety of models: the electron-correlation Mott–Hubbard transition; the Peierls transition in quasi-one-dimensional systems with charge- or spin-density waves; the Verwey transition (as in Fe_3O_4) involving charge ordering; the Anderson transition due to disorder-induced localization, etc [1–3]. In the absence of exact theories, MITs in real systems have been explained (often merely qualitatively) in terms of the available models. For example, for vanadium dioxide there is still no consensus on the description of the driving mechanism of the transition—either electron-correlation effects or structural instabilities [5–9].

On the other hand, the scaling theory of MIT describes the critical behaviour of a system, by analogy with the second-order phase transitions, on the basis of power functions of the coherence length [10]. In general scaling theory, the main idea is that the spatial scale (size) of correlations in a critical region increases infinitely. In this case, details of the system's local behaviour do not play an essential role, and the correlation length ξ, diverging at $T \to T_t$, is the main and the only parameter of the theory [11] (T_t is the transition temperature). The same behaviour of ξ in doped semiconductors is observed at $n \to n_c$, and the value of ξ (on the insulating side) is equal to the localization radius R [10].

It is well known that in the theory of superconductivity (SC) a characteristic scale length (along with the depth of penetration of the magnetic field) is the coherence length [12]:

$$\xi = 2\hbar v_F / \pi \Delta, \tag{2}$$

where $\hbar$ is the Planck constant, $v_F = (\hbar/m)(3\pi^2 n)^{1/3}$ is the Fermi velocity of electrons (m and n are their mass and density, respectively), and Δ is the energy gap width.

In the present paper, on the basis of the Mott criterion, an explicit analytical expression for the correlation length, coinciding formally with the expression (2) for the coherence length in the theory of SC, is obtained. The approach based on the analysis of the correlation length is further used for the description of the MIT in VO_2 with the objective of clarifying the physical mechanism of the transition in vanadium dioxide.

2. Doped semiconductors

In the simplest case of an uncompensated (e.g., n-type) semiconductor, the localization radius coincides with the Bohr radius [2]

$$a_H = \varepsilon \hbar^2 / m^* e^2, \tag{3}$$

where ε is the dielectric constant, and m^* and e are the effective mass and charge of an electron. The gap width for the Mott insulator, in the first approximation, is equal to the energy of ionization of a hydrogen-like impurity $\Delta = I_d = e^2/2\varepsilon a_H$, whence it follows (taking into account equations (1) and (3) with $\xi = a_H$) that

$$\xi = 2\hbar v_F / (3\pi^2)^{1/3} \Delta, \tag{4}$$

which practically coincides with equation (2).

It should be emphasized that the intimate link of the MIT and SC phenomena is well known and has been discussed in the literature [13]. In case of HTSC, for instance, this is connected not

only with the presence of MIT in many metal oxide high-T_c materials, but also with the above-mentioned profound interrelation between SC and MIT. The point is that, if a metal is prone to dielectrization of the electronic spectrum, then this might suppress the transition into the SC state (because of the competition of SC and Peierls instability), but also it might act in quite the reverse way—i.e. promote the appearance of the HTSC properties [13]. The 'symmetry' of MIT and SC shows itself also in the fact that in one case a metal undergoes a transition into the insulating state (electron–hole pairing), and in another case—into the SC state (electron–electron Cooper pairing). The term 'electron–hole pairing' should be considered broadly here. It implies not only excitonic insulators [14, 15], but, particularly, doped semiconductors too. In the latter case, the ionized donor centres play the role of 'holes'. Moreover, the equation for the gap width of an excitonic insulator is absolutely identical to the corresponding equation of the BCS theory [14], where the Debye frequency is replaced by the plasma frequency and the constant of electron–phonon interaction is replaced by the constant of Coulomb interaction. It is no surprise therefore that the expression for the correlation length for MIT, equation (4), coincides with the formula for the coherence length for SC. The coherence length characterizes the size of a Cooper pair, and $\xi = a_H$ in the insulating phase of a MIT material characterizes the size of an 'electron–hole' pair. The only difference consists in the fact that, in equation (4), the Fermi velocity corresponds to the metal state: $v_F \sim (n_c)^{1/3}$, because in the ground, insulating state (below n_c), there are no free charge carriers and v_F is hence not definite.

3. Vanadium dioxide

The above-described model can be applied also to materials exhibiting the temperature-induced MIT (like in VO_2), and not only to those exhibiting the concentration-induced MIT. Vanadium dioxide at $T < 340$ K is a semiconductor; at $T = T_t = 340$ K the conductivity abruptly increases by 4–5 orders of magnitude, and above the transition temperature VO_2 exhibits metallic properties [2]. It has been shown [16–21] that the transition in such compounds can be initiated by an increase in the free charge carrier density without heating the material up to $T = T_t$—under photo-generation of carriers [18, 19] or in high electric field, due to injection, the Poole–Frenkel mechanism [17, 20, 21], etc. This is accounted for by a field-induced increase in the charge carrier concentration which acts to screen Coulomb electron–hole attraction, leading to the elimination of the correlation Mott–Hubbard energy gap at $T < T_t$ [16]. In particular, such a situation occurs upon switching in thin-film VO_2-based sandwich devices in high fields [17]. Furthermore, many authors consider the switching effect in amorphous semiconductors (chalcogenide glasses) to also be associated with MIT [22, 23]. In the case of switching, however, it is difficult to distinguish the electronic and heat contributions, because one cannot exclude current-induced Joule heating of the sample. Nevertheless, for VO_2 the possibility of the electronically induced MIT has been proved experimentally by means of avalanche carrier injection from Si into VO_2 in the structures Si–SiO$_2$–VO_2 [21]. The value of the critical density n_c has been found to be of the order of n_s—the equilibrium electron density in the conduction band of VO_2 in the low-temperature semiconducting phase at $T \to T_t$.

For VO_2, $n_s = 10^{18}$ cm^{-3} (from the values of the resistivity $\rho \approx 20$ Ω cm and the mobility $\mu \approx 0.3$ cm^2 V^{-1} s^{-1} [2]). Let us compare this value with the n_c calculated from equation (1). For $\varepsilon = 100$ [24] and $m^* = 3m$ [2], this yields $a_H = 17.7$ Å (from equation (3)) and $n_c = 2.8 \times 10^{18}$ cm^{-3}, which is in good agreement with the experimental value (n_s), in spite of the roughness of the estimations and some simplification of the model.

The question arising, however, is: what is the physical meaning of the Bohr radius of 18 Å? Unlike the case for doped semiconductors, the localization radius of an electron on
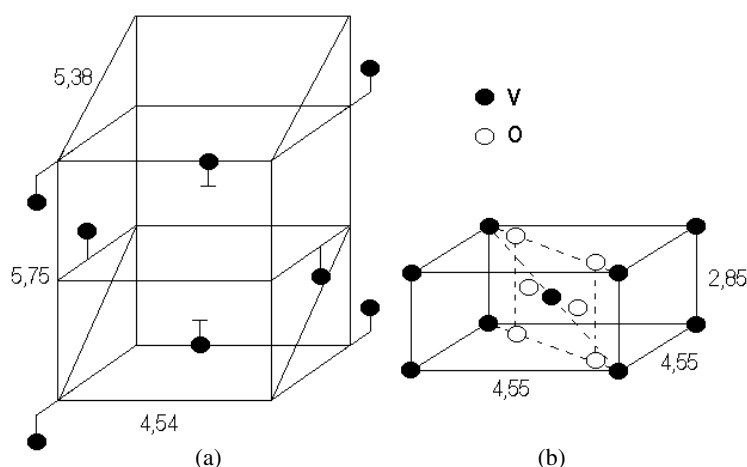
Figure 1. The crystal structure of the semiconductor (a) and metallic (b) phases of VO_2. Distances are indicated in ångströms. Part (a) shows only displacements of the vanadium atoms (schematically). The cell (V_2O_4) volume is 59 $Å^3$.

vanadium atoms, R, is of order 1–3 Å (the atomic radius of vanadium is 1.34 Å [25], and the mean distance V–V in VO_2 is $\sim$3 Å [2]). One can assume that a characteristic length of $\sim$20 Å in this case is just the coherence length, which is not equal to the radius of localization. (Note that the coherence length for MIT in VO_2 was first introduced in [26, 27] by analogy with SC, and the estimate of ξ was there even higher, $\sim 10^{-6}$ cm = 100 Å.)

The point is that the aforementioned analogy with SC—in the case of MIT in transition metal compounds, particularly VO_2—is not absolute. For superconductors $\Delta \approx T_c$, whereas for MIT materials $E_g \neq T_t$. For example, in vanadium dioxide the energy gap width is $E_g = 1$ eV [2], and $kT_t = 0.03$ eV. Therefore $a_H = 18$ Å is just the coherence length, which, as was said above, is not equal to R, i.e. to the size of an electron–hole (or $e^- - V^+$) pair.

The reason for this discrepancy, as we will see in the next section, is that the transition in VO_2 occurs in two stages. Firstly, when the temperature reaches $T = T_t$ (or at $n = n_c$), an electronic Mott transition occurs, which then immediately initiates a distortion of the crystal structure (figure 1) with the symmetry change from monoclinic to tetragonal [2, 5]. The structurally conditioned band gap is $E_g \sim 1$ eV, and the correlation-induced contribution to this value is only $\Delta \approx kT_t$. Thus, the Mott transition in the electron subsystem plays the role of a 'trigger mechanism', which then initiates the structural (Peierls-like) phase transition.

4. Dual transition

We next support these speculations with direct calculations of ξ for VO_2 from equation (4). For $\Delta \sim kT_t$ (more exactly, $\Delta = (2\pi/\gamma)kT_t = 3.53kT_t$ [15] with $\ln \gamma = 0.577$ being the Euler constant), the result must be close to $a_H = 18$ Å. On the other hand, for $\Delta = E_g = 1$ eV, that same formula should result in a ξ-value of the order of $R \sim 2$ Å. For the calculation of v_F we need to know the value of $n = n_m$, the metal-phase electron density, which, unlike for doped semiconductors, is not equal to n_c. In metallic VO_2, one V atom donates one free electron to the conduction band. Indeed, each ion of pentavalent vanadium gives five electrons for chemical bonds; four of them complete p shells of two O^{2-} ions, and the number of band

electrons is thus $5 - 4 = 1$. Then it is straightforward to calculate the density n_m knowing the vanadium dioxide specific gravity (4.34 g cm^{-3} [25]) or the unit-cell volume (see figure 1). These calculations yield $n_m = 3.3 \times 10^{22}$ cm^{-3}, which is in quite good accordance with the estimate of n_m from the conductivity jump: $n_m = (10^4 – 10^5) \times n_s = 10^{22} – 10^{23}$ cm^{-3}.

From equation (4), with $n = 3.3 \times 10^{22}$ cm^{-3}, $m^* = 3m$, and $T_t = 340$ K, the correlation length is $\xi = \xi_1 = 15.7$ Å, which is actually very close to the value obtained above (section 3): $a_H = 17.7$ Å. On the other hand, for $\Delta = E_g$, we obtain $\xi = \xi_2 = 1.62$ Å, i.e. of the order of R. Note that, unlike in the scaling theory of MIT for doped semiconductors, for which the difference between the values of ξ on the metallic and insulating sides of the transition is due to compensation [10], in our case the presence of two coherence lengths is associated with the special nature of the transition in vanadium dioxide. This specific feature consists in the fact that the MIT in VO$_2$ is not a purely electronic Mott–Hubbard transition. Nor is it a purely structural Peierls transition [5, 6, 21]. Basically, the transition involves a complex superposition of these two mechanisms.

The transition in VO$_2$ from a metal ($\Delta = 0$, $\xi \to \infty$) to a semiconductor ($\Delta = E_g$, $\xi = R$), with decreasing temperature, might be imagined as occurring through an intermediate (virtual) state with $\Delta \sim kT_t$ and $\xi = \xi_1 = 15$–20 Å. The modulation of the electronic spectrum at this point results in a Peierls-like distortion of the crystal structure accompanied by doubling of the lattice period (see figure 1(a)). This structural transition, in turn, results in the complete stabilization of the insulating state with $E_g = 1$ eV and complete localization of electrons on vanadium atoms. The intermediate state can be (conditionally) considered as a state in which the electrons are localized only partly. In this case the localization radius (exactly R, not the coherence length ξ_1) can be estimated from the following considerations. As has been noted in [4], for the description of a bound state, the expression for R via the ionization energy (I_d for a donor semiconductor) is more adequate than that via the effective mass, i.e. $R = e^2/2\varepsilon I_d$. For the intermediate state of VO$_2$, I_d corresponds to the value of the correlation gap kT_t, and R will therefore be equal to 2.5 Å, which is approximately equal to the above estimate of R (or $\xi_2 = 1.6$ Å) for the 'complete' insulating state.

The authors of [8] have arrived at the same conclusion about the MIT in VO$_2$ on the basis of the data on temperature hysteresis. In this work, it has been shown that the MIT in vanadium dioxide behaves like an electronic phase transition, i.e. that its initial stage is the rearrangement of the electron system, and the changes inevitably appearing at this point in the crystal lattice are only secondary. It should be noted that such a two-stage mechanism of MIT is not a unique characteristic of vanadium dioxide. A similar situation arises in SmS [28, 29], in which the transition also occurs in two stages—first, in the electron subsystem, and then in the ion subsystem with the change of the crystal lattice parameter.

It is noticeable that the first stage of the MIT in SmS obviously displays the features of the Mott transition[1] which is confirmed by the equality of a_H and the Debye screening length at $T = T_t$ [29]. This transition occurs at a critical density n_c (which, as one can judge from the data of [28, 29], obeys the criterion (1)) under the action of either pressure or temperature. Similarly, in VO$_2$ the MIT occurs at a certain $n = n_c$, and it does not matter in what way this transition is initiated—either under heating up to $T = T_t$ (i.e. as the result of the equilibrium thermal generation of carriers), or under photo-generation [18, 19], injection [21], or high-field generation at switching [17, 20].

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[1] Such a description of the transition on the whole is surely oversimplified. A more sophisticated model of the MIT in the rare-earth-metal mono-sulfides (chalcogenides) is based on the specific properties of f electrons (see 4.11 in monograph [2], as well as [28, 29] and references therein).

5. Conclusions

In concluding, we comment on the terminology used, namely on the terms 'coherence length' and 'correlation length'. In most papers concerning the problem of MIT (and in the present one, as well) the two terms are used alternately, as equivalent to each other. Meanwhile, the term 'coherency' relates, apparently, only to superconductors, in which the electron system is described by a unique wavefunction in the ground state (below T_c). For other phase transitions (including the MIT) this is not the case. However, as shown above, this fact does not prevent the use of the term 'coherence length' (at least, formally—bearing in mind the correlation length) for the analysis of a physical mechanism of the transition.

Thus, in the present work the expression for the correlation length, coinciding formally with the expression for the coherence length in the theory of SC, was obtained from the Mott criterion. This relation was used to calculate ξ for vanadium dioxide; it was shown that there exist two distinct coherence lengths. This is associated with the dual nature of the transition, and the driving mechanism of the MIT in VO_2 is the electronic Mott–Hubbard transition. The electron-correlation contribution to the energy gap, corresponding to this transition, is^2$\Delta \sim kT_t \sim 0.1$ eV and $\xi = 15$–20 Å. The modulation of the electronic spectrum results then in distortion of the crystal structure accompanied by formation of the gap $\Delta \sim E_g$ and by the complete localization of electrons onto vanadium atoms ($\xi = 1$–2 Å).

This structural transition is therefore not a reason, but is a consequence of the electronic transition, as has been repeatedly confirmed experimentally [8, 19, 21].

Moreover, it appears that it is not even necessary for this electronic MIT in VO_2 to be accompanied by a structural change [30]. It is likely that this situation might take place when, e.g., the MIT is initiated by picosecond and femtosecond laser pulses [18, 19], i.e. under non-equilibrium conditions with possible formation of a metastable metallic phase. At least, as has been noted in the work [19], 'in this regime, the structural transition may not be thermally initiated'. In fact, it is truly remarkable that the structural transformation can proceed at all in this regime (for $t \sim 10^{-13}$–10^{-14} s!) Nevertheless, whatever it is, these experiments convincingly support the main emphasis of our conclusion—that is, that the structural transition may not be a first-cause impetus for the MIT in vanadium dioxide.

Acknowledgments

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^{2} This value is much less than $E_g = 1$ eV; therefore there is no contradiction with the conclusion of the work [9] that 'the electronic structure of VO_2 is more band-like than correlated'.

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