# Intermediate state of materials experiencing a semiconductor–metal phase transition

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Crystals exhibiting an insulator–metal phase transition of the first kind may undergo an intermediate state in which both phases are intermixed. In particular, this may explain several peculiarities in the behavior of materials with mixed valency.

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It is known that certain materials may occur in a heterophase state in which different phases are mixed with one another (e.g., the intermediate state of superconductors,[1] and the ferro-antiferromagnetic state of degenerate magnetic semiconductors[2]). It will be shown below that for materials displaying an insulator–metal phase transition, an intermediate state is also possible in which the conducting and insulating phases are mixed together. As is the case for magnetic semiconductors, this state is caused by the charging of regions of different phases relative to one another, leading to a negative surface phase interface energy $\alpha$, making their mixture thermodynamically favorable.

Actually, $\alpha$ consists of a part $\alpha_e$ due to the migration of the electrons across the phase interface as a result of which a dual electrical layer arises, and a part $\alpha_0$ due to remaining physical factors. The value of $\alpha_e$ is always negative since the migration of electrons across the interface occurs only because this is a thermodynamically favorable process. It is determined by the difference of the electron work function $W$ in the metallic and insulating phases, which may be displaced by 0.1–1 eV by alloying. The value of $\alpha_0$ is positive and insensitive to alloying. The sum $\alpha_e + \alpha_0$ may be negative even in a pure crystal, or else it may be made so by alloying the crystal.

There are experimental data[3,4] which indicate the occurrence of inclusions of a highly-conducting phase significantly below the point $T_t$ in the transition of $VO_2$ from an insulating to a highly-conducting state. However, additional studies are needed to prove that these inclusions are not caused by the inhomogeneity of the samples. The intermediate insulator–metal state hypothesis also explains why SmS crystals for $T \to 0$ and pressures above 10 kbar possess, it would seem, mutually exclusive properties: a high electron heat capacity at low electrical conductivity (see the review[5]).

Instead of calculating $\alpha_e$, we shall calculate the change in the free energy of the system $F$ during the formation of a metallic sphere of radius $R$ within the semiconductor phase below $T_t$. Without calculating the charge transfer, the free energy should increase by $\sigma F_0$ because of the increase of its volumetric part by $\delta f$ per unit volume, its surface energy $\sim \alpha_0$, and its lattice deformation energy (in an isotropic model the latter quantity is calculated as in Ref. 6):

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$$\delta F_o = \frac{4\pi}{3} R^3 g + 4\pi R^2 a_o ,$$

$$g = \delta f + \frac{E\omega^2}{9(1-\sigma)} , \tag{1}$$

where $\alpha$ is the lattice constant, $E$ is Young's modulus, $\sigma$ is the Poisson coefficient, and $\omega$ is the relative volume change during the phase transition.

The change in free energy $\delta F_e$ due to the transfer of electrons from one phase to the other will be calculated for the special case of a crystal with a large concentration of donor impurity $n$. It is assumed that $W > 0$. Then, the electrons of all the donors lying within the spherical layer $R < r < R_W$ transfer from the semiconductor phase to the metallic one. The radius $R_W$ should be found from the condition for the minimum of $\delta F_e$.

We shall assume that $R$ significantly exceeds the minimum radius $R_m$ at which the level occurs within the spherical potential well of depth $W$, but that $R$ is comparable with the screening radius in the high-conductivity phase $R_s$. The condition $R_s \gg R_m$ is satisfied if the high-conductivity phase is a semimetal, in particular, for $VO_2$ in which the carrier density is $\sim 10^{21}$ cm$^{-3}$.[7] It is then natural to approximate the excess electron density in the sphere $n_d$ by a constant. Calculating the energy of the electrostatic charge coupling similarly to what was done in Ref. 4, under the condition that the charge $Q$ which had migrated into the sphere is large in comparison with the donor charge $Q_0$ inside it, we obtain

$$\delta F_e = \frac{Q^2}{2R\tilde{\epsilon}} - \frac{Q}{e} W, \qquad \frac{1}{\tilde{\epsilon}} = \frac{1}{\epsilon} + \frac{1}{5\epsilon_o} ,$$

$$Q = \frac{4\pi}{3} ne(R_W^3 - R^3) = -\frac{4\pi}{3} n_d e R^3; \qquad Q_o = \frac{4\pi}{3} neR^3 , \tag{2}$$

where $\epsilon_0$ and $\epsilon$ are the permittivities of the high- and low-conductivity phases, respectively. The correction to the surface energy due to the quantization of the motion of the electrons which have migrated to the sphere, calculated from the results in Ref. 4, here turns out to be negligibly small.

Minimizing the total change in free energy $\delta F = \delta F_0 + \delta F_e$ in terms of $Q = Q(R_W)$ and $R$, we obtain their optimal values from Eqs. (1) and (2)

$$\delta F = -\frac{4\pi}{3} (K-1)^2(2K+1) \frac{a_o^3}{g^2} ,$$

$$R = \frac{a_o}{g} (K-1) , \quad Q = \frac{WR\tilde{\epsilon}}{e} , \quad K = \left[1 + \frac{W^2\tilde{\epsilon} g}{8\pi e^2 a_o^2}\right]^{1/2} . \tag{3}$$

Therefore, if the conditions $R \gg R_m$ and $Q \gg Q_0$ are satisfied, the formation of a high-conductivity sphere actually lowers the free energy of the system. On lowering the temperature, i.e., with increasing $g$, the radius $R$, charge $Q$, and the gain in free energy $(-\delta F)$ all decrease. For $R \simeq R_m$, the formation of the sphere is even more thermodynamically unfavorable.

When the formation of a single sphere encompasses only a region of the crystal with radius $R_W$, for $\delta F < 0$, the entire crystal should be partitioned into regions with size $\sim R_W$, inside each of which is located a high-conductivity region of radius $\sim R$, i.e., the crystal should be in an inhomogeneous state that is intermediate between high- and low-conductivity states. If the degree of thermal ionization of the impurity is small, $W$ will be independent of $n$. Then, $R$ and $Q$ from Eqs. (3) also are independent of $n$, while $R_W$ [Eq. (2)] decreases with increasing $n$, i.e., the number of inclusions of the high-conductivity phase increases with $n$.

In order to show the reality of the intermediate state, we shall calculate $R$ and $Q$ at $T_t$, using typical values for the parameters $W = 1$ eV, $\alpha_0 = 10$ erg/cm$^2$, $\omega = 0.01$, $E = 2 \times 10^{11}$ erg/cm$^3$, $\sigma = 0.3$, $\epsilon_0 = 5$, and $\epsilon = 30$ (for example, $VO_2$ has $\epsilon$ tensor components equal to 19 and 39 [8]). Then, from Eq. (3) we obtain $R = 20$ Å and $Q/e = 30$, i.e., actually $R \gg R_m \sim \overset{\circ}{a}$, and for $n \lesssim 10^{20}$ cm$^{-3}$ the inequality $Q \gg Q_0$ is satisfied. In any case, $R = 30$ Å does not contradict the value $R < 3000$ Å obtained experimentally for $VO_2$.[3]

It should be emphasized that the assumption concerning the significant concentration of defects of the required type (donors for $W > 0$, acceptors for $W < 0$) was made earlier only to insure the maximum in $|W|$. In principle, the intermediate state is possible even in unalloyed crystals, although for them $|W|$ is smaller. In the latter case, alloying with impurities of one sign increases, and with the other sign decreases, the stability of the intermediate state. Of course, it is conceivable that such a state is not possible in general either in pure or alloyed crystals, i.e., for any practically attainable degree of alloying $\alpha > 0$. In this case, alloying with those impurities which decrease $|W|$ will lead to one more unusual effect: it increases $\alpha$ and, consequently, makes it difficult to form the nucleus of a new phase in a phase transition of the first kind. The situation here stands in contrast with the usual situation, where the introduction of defects facilitates the formation of a new phase.


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