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# The photoinduced Mott transition from metal to insulator: the problem of critical concentration

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## Abstract

The non-equilibrium (photoinduced) phase transition from a metal (M) state to a semiconducting (S) state is discussed using the example of samarium monosulfide. An expression for the critical concentration, analogous to the Mott criterion, is obtained. It is shown theoretically that the critical electron density for such a M → S transition should be of the order of, or little less than, the equilibrium density in the metallic phase beyond the transition point. Some relevant experimental data concerning the metal–insulator transitions in SmS and VO<sub>2</sub> are discussed.

Inducing and probing non-thermal phase transitions in solids using femtosecond laser pulses is a relatively new and rapidly advancing research direction in condensed matter physics [1, 2]. In particular, the study of photoinduced metal–insulator transitions (MIT) in strongly correlated systems is of importance for better understanding the transition mechanism [3]. Previously, the photoinduced MITs in the femtosecond regime have been studied in VO<sub>2</sub> [3–5], Ti<sub>2</sub>O<sub>3</sub> [6], A3B5 semiconductors [7], and SmS [8]. It is noteworthy that, in samarium monosulfide, the laser irradiation can also initiate a transition from the metal phase to the semiconducting one (M → S) [8], unlike in the other materials listed, for which only a photoinduced semiconductor-to-metal (S → M) transition has been reported [3–7].

The standard (S → M) electronically induced Mott transition occurs at a certain critical electron density  $n = n_{c1}$ , and it does not matter in what way this density is created—either as the result of equilibrium generation of carriers under the action of temperature or pressure, or under photo-generation, injection from contacts, or high-field generation at switching [9]. The critical concentration is given by the Mott criterion [10]:

$$a_H n_{c1}^{1/3} = 0.25, \quad (1)$$

where  $a_H = \frac{\hbar^2 \epsilon}{m^* e^2}$  is the effective Bohr radius ( $\epsilon$ —the dielectric constant;  $m^*$ —the effective mass). Since the MIT in SmS is certainly an electronically induced transition (albeit more

complicated than a simple Mott transition) [8, 10, 11], there arises the question of whether a relation similar to equation (1) exists for such a  $M \rightarrow S$  MIT, and also—what is the value of the critical concentration (we denote it as  $n_{c2}$ ) in this case?

For SmS, it has been shown [8] that a femtosecond laser pulse ( $\tau = 120$  fs) induces the photoreduction of Sm ions; the electrons from 5d levels of Sm ions are excited up to the vacuum level, and then re-trapped at the 4f level. As a result, this 5d–4f transition causes the phase transition from M- to S-SmS. Apart from the case for SmS, the problem outlined above might be related to possible photoinduced transitions in materials exhibiting inverse MITs<sup>3</sup>: e.g.,  $V_2O_3$  doped with Cr,  $NiS_{2-x}Se_x$ , nonstoichiometric EuO, and manganites  $R_{1-x}A_xMnO_3$  (where R is a rare-earth cation and A is an alkaline-earth cation) [10, 12]. In particular, the relaxation dynamics of charge carriers in  $La_{0.7}Ca_{0.3}MnO_3$  has been recently studied by the light reflection method with a femtosecond time resolution [13].

The objective of this paper is to investigate the question posed above and to further elaborate the approach to the description of the Mott transition developed previously in the work [9].

It has been shown [10] that the carrier concentration  $n_{c1}$ , given by equation (1), is necessary to give enough screening to ensure that the screened Coulomb potential leads to no bound state. A simple and clear way to deduce equation (1) is to consider the condition  $L_D \leq R$  [14] for the  $S \rightarrow M$  transition to occur, where  $L_D = (\pi a_H / 4k_F)^{1/2}$  is the Debye screening length and  $R$  is the localization radius coinciding with  $a_H$  for semiconductors [9]. This picture is very qualitative and ignores some fundamental aspects of the MIT (particularly, the magnetic interactions [12]), but it nonetheless gives a correct value of the constant in the right-hand side of equation (1). In doped semiconductors, the transition is controlled by the dopant concentration  $N$  (in uncompensated semiconductors  $n = N$ ) and  $n_{c1} \approx n_{c2}$ ; fine differences between these two parameters, connected with compensation and specific band structure peculiarities, have been recently discussed in [15]. In compounds of transition and rare-earth metals, the process is controlled (in equilibrium) by temperature or pressure and, in this case,  $n_{c1} \neq n_{c2}$ —see figure 1. For the equilibrium temperature- or pressure-driven transition,  $n_{c2} \approx n_m$ , the metal phase electron density. It is obvious that for the non-equilibrium  $M \rightarrow S$  transition, driven by photoexcitation or injection<sup>4</sup>, the value of  $n_{c2}$  should also be approximately equal to, or a little less than, the concentration in the metallic state; at least,  $n_{c2} > n_{c1} = n_s$ , where  $n_s$  is the equilibrium electron density in the semiconducting phase at  $T \rightarrow T_i$  or  $P \rightarrow P_i$ . It is pertinent to note that the above-discussed difference between these two parameters, i.e.  $n_{c1}$  and  $n_{c2}$ , is intimately linked to the cooperative nature of the MIT.

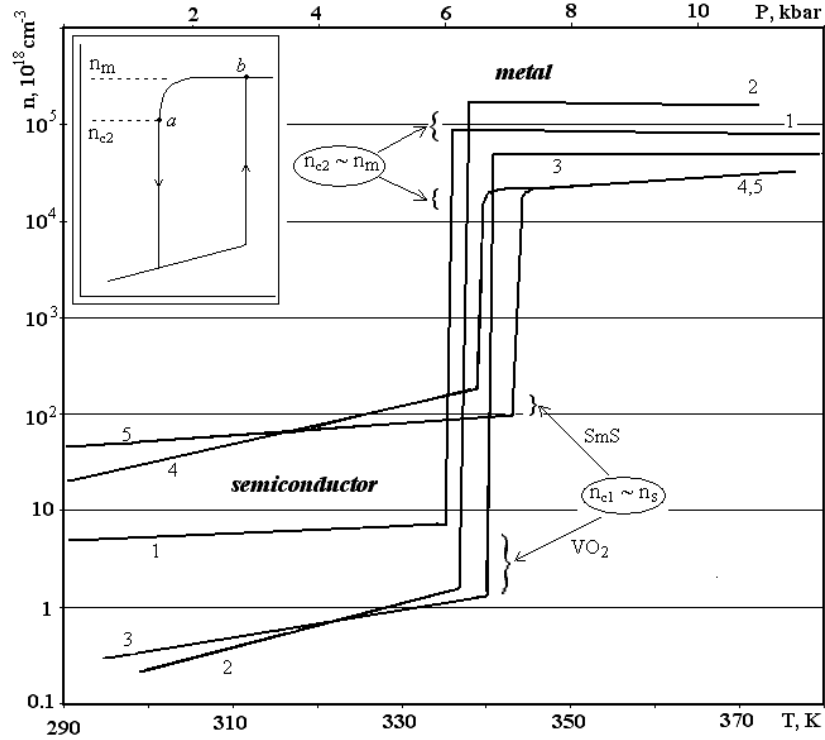
To derive an equation for  $n_{c2}$ , we again use the condition  $L_D = R$ , but now  $R \neq a_H$ , because, for the metal state, the concept of Bohr radius makes no sense. For the  $M \rightarrow S$  transition, as the electron density  $n$  in a metal is decreased, screening falls ( $L_D$  rises), and when  $L_D$  reaches the value of  $R$ , all the electrons will be trapped at the ionic sites. For the ‘dual transition’ (as in  $VO_2$  and SmS [9]), this  $R$  corresponds to the intermediate state.

It has been shown [9] that for the intermediate state of the dual transition in  $VO_2$ , the localization radius  $R$  is equal to the coherence length  $\xi_2$  in the ground semiconducting state:

$$\xi_2 = 2\hbar v_F / [(3\pi^2)^{1/3} E_g], \quad (2)$$

<sup>3</sup> Usually, the low-temperature phase is insulating, and on heating above the transition temperature  $T_i$  (or, as in SmS, by applying a pressure  $P > P_i$ ), the material becomes metallic [10]. For the inverse (or re-entrant) MIT, in contrast, the insulating phase is high temperature, and the ground low-temperature state is metallic.

<sup>4</sup> The photoinduced  $M \rightarrow S$  transition can be experimentally observed, as discussed above, in SmS [8], as well as, presumably, in materials exhibiting a re-entrant MIT; in other transition metal compounds, e.g. in  $VO_2$ , the non-equilibrium  $M \rightarrow S$  transition can be realized by means of hole injection to (electron extraction from) the metal phase. Unlike in the simple metals, this process is feasible in the correlated metals, because they behave, in some sense, like degenerate semiconductors.



**Figure 1.** Electron density as a function of temperature (for VO<sub>2</sub>, curves 1–3, lower axis) or pressure (for SmS, curves 4 and 5, upper axis). The data for VO<sub>2</sub> are calculated using the  $\rho(T)$  dependences ( $\mu = 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [10], and those for SmS are adopted from [11]. Only the curves obtained on heating (pressure increase) are shown, and hysteresis behaviour is illustrated in the inset. For VO<sub>2</sub> the hysteresis loop is normally 5–10 K [10], and for SmS it is rather wide, up to  $\sim 5$  kbar [11].

where  $v_F = (\hbar/m^*)(3\pi^2 n_m)^{1/3}$  is the Fermi velocity of electrons in the metal state and  $E_g$  is the energy gap width in the semiconducting state. The expression for the screening length can be written in the form

$$L_D = (\pi[\varepsilon\hbar^2/m^*e^2]/4k_F)^{1/2}, \quad (3)$$

where  $k_F = (3\pi^2 n_{c2})^{1/3}$  is the Fermi wavevector at  $n = n_{c2}$ , and  $\varepsilon = \varepsilon_\infty$  and  $m^*$  both now relate to the metal state, unlike those in the case of the Bohr radius in equation (1). The condition  $L_D = \xi_2$ , taking into account equation (3) and the equality  $\xi_2 = R$ , can be written as  $\frac{\pi[\varepsilon\hbar^2/m^*e^2]}{4(3\pi^2 n_{c2})^{1/3}} = \xi_2^2$  or  $Rn_{c2}^{1/3} \approx 0.25 \frac{\varepsilon\hbar^2/m^*e^2}{\xi_2}$ . From the latter equation, substituting  $\xi_2$  from equation (2) into the denominator, it is straightforward to show that

$$Rn_{c2}^{1/3} \approx 0.25 \frac{E_g}{W}, \quad (4)$$

where  $W = 2e^2/\varepsilon(n_m)^{-1/3}$  is the average potential Coulomb energy of an electron in the metal phase. For VO<sub>2</sub>,  $\varepsilon_\infty \approx 9$  [16],  $n_m = 3.3 \times 10^{22} \text{ cm}^{-3}$  [9], and  $W \sim 1 \text{ eV}$ . Since  $E_g$  for vanadium dioxide is also of the order of 1 eV ( $\sim 0.7 \text{ eV}$  [10, 16]), the criterion (4) is thus absolutely equivalent to the Mott criterion (1), the only difference being that  $R \ll a_H$  and, consequently,  $n_{c2} \gg n_{c1}$ . Note that the correlation  $W \approx E_g$  is characteristic of all the strongly correlated systems, not only of VO<sub>2</sub>; therefore the constant in the right-hand side of

**Table 1.** Electron densities in VO<sub>2</sub> and SmS.  $n_{c1}$ ,  $n_{c2}$ —the critical values for the S → M, equation (1), and M → S, equation (4), transitions;  $n_s$ ,  $n_m$ —the equilibrium parameters of the semiconducting and metallic phases, respectively, in the vicinity of the transition point;  $n_{ex}$ —upper estimates of the experimental values for the fs laser-induced S → M (VO<sub>2</sub>) and M → S (SmS) transitions.

$n$ (cm <sup>-3</sup> )	$n_{c1}$	$n_s$	$n_{c2}$	$n_m$	$n_{ex}$
VO <sub>2</sub>	$2.8 \times 10^{18}$ [9]	$10^{18}$ – $10^{19}$ [10] (see figure 1)	$1.1 \times 10^{22}$	$3.3 \times 10^{22}$ [9]	$(1\text{--}5) \times 10^{21}$ [4]
SmS	$(0.8\text{--}1.8) \times 10^{20}$ [19]	$2 \times 10^{20}$ [11]	$1.2 \times 10^{21}$	$1.5 \times 10^{22}$ [11]	$3.4 \times 10^{22}$ [8]

equation (4) does not differ too much from the value 0.25. In the case of vanadium dioxide, using the values  $R = 0.8 \text{ \AA}$  (the average ion radius of vanadium, i.e. the radius of the vanadium d shell) [17] and  $E_g = 0.7 \text{ eV}$ , equation (4) yields  $n_{c2} = 1.1 \times 10^{22} \text{ cm}^{-3}$ .

One can see that, indeed,  $n_{c2} > n_{c1} \sim n_s$ . On the other hand, the theoretical value of  $n_{c2}$  obtained does not coincide exactly with  $n_m$  (see figure 1):  $n_{c2}$  is a factor of three less than  $n_m$ , which might be explained by the hysteresis, as depicted by the inset in figure 1. It is clear that the underlying physics of the difference between  $n_{c2}$  and  $n_m$  is not directly associated with the hysteresis as such. This figure (the inset) is intended merely to illustrate the fact that the density  $n_{c2}$ , which corresponds to the commencement of the M → S MIT (point *a*), is little less (or, perhaps, considerably less) than the equilibrium density in the metallic phase beyond the transition (point *b*). What is the reason for such behaviour and how large is the value of  $\Delta = |n_{c2} - n_m|$ ? This problem is still to be clarified. In any case, this  $\Delta$  is surely not a very large value, even if is equal to about an order of magnitude. The point is that we deal with the materials in which the electron concentration jump ( $n_m/n_s$ ) is usually of many orders of magnitude. Probably, VO<sub>2</sub> and, especially, SmS are not the very good examples in this sense. However, in V<sub>2</sub>O<sub>3</sub>, for instance,  $n_m/n_s$  is  $\sim 10^7$ , and in EuO the electrical conductivity changes even by a factor of up to  $10^{19}$  (!) [10, 12].

Also, one can surmise that the region between  $n_{c2}$  and  $n_m$  just corresponds to the above-mentioned intermediate state of the dual MIT in VO<sub>2</sub> [9].

Next we consider the case of samarium monosulfide. Taking  $\varepsilon_\infty \approx 4$  (the dielectric permittivity of M-SmS at  $\omega \sim \omega_p$ , the plasma frequency) [18] and  $n_m = 1.5 \times 10^{22} \text{ cm}^{-3}$  (figure 1, curve 4), we obtain  $W \sim 1.8 \text{ eV}$ . Now, using the values of  $R = 0.3 \text{ \AA}$  (the radius of the samarium 4f electron shell) and  $E_g = 0.23 \text{ eV}$  (the gap between the 4f level and the conduction band) [11], equation (4) yields  $n_{c2} = 1.2 \times 10^{21} \text{ cm}^{-3}$ . Once again, like in the case of VO<sub>2</sub>, this  $n_{c2} > n_{c1}$  ( $\sim 10^{20} \text{ cm}^{-3}$ —see table 1) or  $n_s = 2 \times 10^{20} \text{ cm}^{-3}$ , but  $n_{c2}$  is almost an order of magnitude lower than  $n_m$ . Certainly this discrepancy might be attributed to some inaccuracy of our rather rough evaluations. However, this might also mean that the genuine M-to-S transition actually commences at  $n \sim n_{c2}$ , which is smaller than  $n_m$ , as was discussed above in relation to vanadium dioxide.

The minimum number of the excited electrons  $n_{ex}$ , required to initiate the M → S transition in SmS, is  $n_{min} = (n_m - n_{c2}) \sim n_m$ . The experimental value of  $n_{ex}$  can be easily calculated from the data of [8]:

$$n_{ex} = \frac{(1-r)E}{h\nu d}, \quad (5)$$

where  $r = 65\%$  [8, 18] is the reflection of metallic SmS,  $E = 0.5 \text{ J cm}^{-2}$  the laser energy, and  $h\nu = 1.6 \text{ eV}$  for  $\lambda = 800 \text{ nm}$  the laser wavelength;  $d \sim 200 \text{ nm}$  is the thickness of a layer wherein the absorption occurs for the most part [8]. In equation (5), we did not take into consideration the processes of diffusion and recombination (generally reducing the value of  $n_{ex}$ ) which are apparently negligible for a pulse duration of 120 fs, because in such materials

the relaxation of the excited electrons should occur typically on a timescale slower than a few hundred femtoseconds [1]. Equation (5) yields thus  $n_{\text{ex}} = 3.4 \times 10^{22} \text{ cm}^{-3}$ , which is well above the density  $n_{\text{min}} \sim 1.5 \times 10^{22} \text{ cm}^{-3}$  indispensable for the transition to occur; that is, the value of  $E$  appears to exceed a minimum threshold energy  $E_0$ . If however the recombination time is comparable to the pulse duration ( $\sim 10^{-13}$  s), then equation (5) gives an overestimated value of  $n_{\text{ex}}$ . For example, in the case of  $\text{VO}_2$ , the value of  $n_{\text{ex}}$  has been estimated directly from the number of absorbed photons per unit volume [4], i.e., in fact, from a formula similar to equation (5).

It should be noted however that we have confined our attention solely to the static case, and an analysis of temporal dynamics [1] for the MIT at  $n_{\text{ex}} \rightarrow n_{\text{cl},2}$  is the problem subject to further exploration. Summarizing, all the above-discussed data are gathered in table 1, which compares theoretical values of the critical concentrations with observed equilibrium concentrations on either side of the transition.

Thus, the electronically induced  $\text{M} \rightarrow \text{S}$  transition in SmS has been observed experimentally and, as is shown above, it may be described in terms of the Mott transition (we emphasize once again that the transition mechanism is similar, but not identical, to the simple Mott transition). In this context, it would also be interesting to realize the non-equilibrium (i.e. occurring not under pressure)  $\text{S} \rightarrow \text{M}$  MIT in samarium monosulfide. However, as far as we know, only one indication of that (namely, the temperature-induced generation of thermo-emf) has been reported in the literature to date [19].

The equilibrium pressure-induced MIT in SmS can be described as follows [8, 10, 11, 18, 19]. With increase in pressure, the lattice constant of SmS decreases and a reduction in the energy gap between the 4f states and the 5d conduction band occurs. Ionization of the localized f levels leads to an increase of the free electron density and hence to an increase of screening. This, in turn, results in further increase of the ionization degree, further diminishing of  $E_g$  [10], and, finally, in the elimination of the energy gap at  $P = P_t$ . The situation is thus reminiscent of the Mott MIT in doped semiconductors, with the Sm 4f levels playing the role of donor levels [11]. On the other hand, similarly to the case for  $\text{VO}_2$ , the MIT in SmS occurs in two stages [19]—first, in the electron subsystem (accompanied by the change of the samarium ion valency  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$ ), and then in the ion subsystem with the change of the crystal lattice parameter from 5.97 to 5.70 Å [11, 18, 19].

Thus, the MIT in SmS can be initiated not only under the action of pressure (i.e. in an equilibrium way), but it can also be initiated in any other (non-equilibrium) way with an increase in electron density up to  $n = n_{\text{cl}}$ , because the electrons in the conduction band will screen the f levels, irrespective of how these electrons have appeared—due to either band overlapping, or thermal excitation [10], or any other excitation. In particular, if it is possible that the 4f–5d transition is induced by ultrafast laser pulses, this phase transition can occur at high speed without thermal stress and ablation [8]. Such studies, along with the investigation of structural dynamics, would allow elucidation of the physical mechanism of the transition in samarium monosulfide. Note that the generation of femtosecond x-ray pulses has recently become possible and enabled a sub-picosecond time resolution of x-ray spectroscopy [20, 21]. Ultrafast x-ray diffraction combines atomic scale spatial and temporal resolution enabling extremely rapid changes in the atomic configuration to be directly observed.

In particular, the combination of optical pump–probe spectroscopy, using femtosecond laser pulses, with femtosecond x-ray spectroscopy has been recently applied to investigation of the MIT in  $\text{VO}_2$  [3, 4]. It was shown that the electronic structure of the semiconducting phase is more band-like than correlated, which is in agreement with the band structure calculations for vanadium dioxide [16]. (Note that this fact does not contradict an electronically driven Mott transition mechanism [9].) However, at such a high degree of electronic excitation,

$\sim 5 \times 10^{21} \text{ cm}^{-3}$  [4], a structural realignment (due to either interatomic force modification or coherent phonons [3]) seems to become inevitable [1, 2]. In order to advance our understanding of the transition scenario, it is necessary to realize the simultaneous observation of both electronic structure and atomic structure temporal dynamics in the femtosecond regime and, in addition, as close to the threshold ( $E \sim E_0$ ,  $n \sim n_{c1}$ ) as possible. This, of course, is rather complicated experimentally (especially for thin films), though recent progress in this field and the continued development of experimental techniques [20] allow one to hope that such research will be possible in the near future.

Finally, these studies appear to be necessary, because the phase transitions in SmS and VO<sub>2</sub>, induced by femtosecond laser pulses, can be useful for applications in high-speed optical switches and memory [5, 8].

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