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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **39** (2006) 4619–4623 doi:10.1088/0305-4470/39/17/S48

Photoinduced metal–insulator transitions: critical concentration and coherence length

Alexander Pergament[1] **and Andreas Morak**[2]

[1] Petrozavodsk State University, Petrozavodsk, 185910, Russian Federation
[2] Friedrich-Schiller-University, Max-Wien-Platz 1, 07743 Jena, Germany

E-mail: aperg@psu.karelia.ru and andreas.morak@jenoptik.com

Received 7 September 2005
Published 7 April 2006
Online at stacks.iop.org/JPhysA/39/4619

Abstract
The photoinduced re-entrant metal-to-insulator transition is considered. Using the concept of coherence length, an equation for the critical concentration, similar to the Mott criterion, is obtained. Experimental results are discussed concerning the metal–insulator transitions in SmS and VO_2.

PACS numbers: 71.30.+h, 72.80.Ga, 78.47.+p, 05.70.Ln, 05.70.Fh

Strongly correlated electrons in solids, characterized by a significant ratio of the Coulomb potential energy to the electron kinetic (Fermi) energy, are a special case of strongly coupled Coulomb systems. Strong correlation effects are responsible for the unique properties of materials such as high-T_c superconductors, manganites with colossal magnetoresistance (CMR) and materials with metal–insulator transition (MIT). MIT, in turn, is a problem of considerable interest [1, 2], being concerned with a wide range of issues in plasma physics, astrophysics and condensed matter physics. On the other hand, inducing and probing non-thermal phase transitions in solids using femtosecond laser [3] and x-ray [4] pulses is nowadays a relatively new and rapidly advancing research direction. In particular, the study of photoinduced metal–insulator (or metal–semiconductor) transitions in strongly correlated systems is of importance for better understanding the transition mechanism [5]. The photoinduced MITs in the femtosecond regime have been studied, for example, in GaAs and GeSb [6], Ti_2O_3 [7], VO_2 [5] and SmS [8].

It is important to emphasize that in samarium monosulfide the laser irradiation can 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 [5–7]. 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 [1, 10]:

$$a_H n_{c1}^{1/3} = 0.25, \tag{1}$$

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where

$$a_H = \frac{\hbar\varepsilon}{m^* e^2} \tag{2}$$

is the effective Bohr radius, $\hbar$ the Planck constant, ε the material dielectric permittivity, m^* and e the effective mass and charge of an electron.

For metallic SmS, femtosecond laser pulses have been shown to induce the photoreduction of Sm ions [8]; 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. Usually, the low-temperature phase is insulating, and above the transition temperature T_t the material becomes metallic; for the inverse MIT, in contrast, the insulating phase is high-temperature, and the ground low-temperature state is metallic. Such inverse (or re-entrant) MITs are observed, e.g., in $(V_{1-x}Cr_x)_2O_3$, $NiS_{2-x}Se_x$, nonstoichiometric EuO and CMR-manganites [1, 10, 11].

Since the MIT in SmS is certainly an electronically-induced transition (albeit it is more complicated than a simple Mott transition) [8, 10, 12–14], there arises the question of whether a relation similar to equation (1) exists for such M→S MIT, and also—what is the value of the critical concentration (we denote it as n_{c2}) in this case?

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

$$L_D = R \tag{3}$$

for the S→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. This picture is very qualitative and ignores some fundamental aspects of the MIT (particularly, the magnetic interactions [11]), but it nonetheless gives a correct value of the constant on the right-hand side of equation (1); namely, from equation (3) one obtains $a_H n_{c1}^{1/3} = \frac{\pi}{4(3\pi^2)^{1/3}} = 0.254$. In doped semiconductors, the transition is controlled by the impurity concentration N (in uncompensated semiconductors $n = N$) and $n_{c1} \approx n_{c2}$. In compounds of transition and rare-earth metals, the process is controlled (in equilibrium) by temperature or pressure and, in this case, $n_{c1} \neq n_{c2}$—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→S transition, driven by photoexcitation or injection, the value of n_{c2} should also be approximately equal to, or 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 in the vicinity of the transition point, i.e. at $T \to T_t$, or, in the case of a pressure-driven transition, at $P \to P_t$ (in SmS, e.g., $P_t = 6.5$ kbar [12–14]).

In order to deduce an equation for n_{c2}, we again use condition (3), but now $R \neq a_H$, because, for the metal state, the concept of Bohr radius has no sense. For the M→S transition, as the electron density n in a metal is decreased, screening falls (L_D rises), and when L_D will reach the value of R, all the electrons will be trapped at the ionic sites. For the 'dual' (or two-stage) 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 ξ_2 in the ground semiconducting state:

$$\xi_2 = \frac{2\hbar v_F}{(3\pi^2)^{1/3}\Delta} \tag{4}$$

where $v_F = (\hbar/m^*)(3\pi^2 n_m)^{1/3}$ is the Fermi velocity of electrons in the metal state, and Δ is

the energy gap width in the semiconducting state. The expression for the screening length one can write in the form:

$$L_D = (\pi[\varepsilon\hbar^2/m^*e^2]/4k_F)^{1/2}, \tag{5}$$

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 (2). The condition $L_D = \xi_2$, taking into account equation (5) and the equality $\xi_2 = R$, can be written as

$$\frac{\pi[\varepsilon\hbar^2/m^*e^2]}{4(3\pi^2 n_{c2})^{1/3}} = \xi_2^2 \qquad \text{or} \qquad Rn_{c2}^{1/3} \approx 0.25\frac{\varepsilon\hbar^2/m^*e^2}{\xi_2}.$$

From the latter equation, substituting ξ_2 from equation (4) into the denominator, it is straightforward to show that

$$Rn_{c2}^{1/3} \approx 0.25\frac{\Delta}{W}, \tag{6}$$

where $W = 2e^2/\varepsilon(n_m)^{-1/3}$ is (approximately) the average potential Coulomb energy of an electron in the metal phase. For VO_2, $\varepsilon_\infty = 9.5$ [15], $n_m = 3.3 \times 10^{22}$ cm^{-3} [9], whence it follows that $W = 0.97$ eV. Because Δ ($= E_g$, the semiconducting energy gap) in vanadium dioxide is also of the order of 1 eV (more exactly, ~0.7 eV [1, 15]), the criterion (6) is almost equivalent to the Mott criterion (1), and the main difference between equations (1) and (6) is that $R \ll a_H$; therefore, $n_{c2} \gg n_{c1}$. For the standard doped semiconductors, the gap in equation (4) is equal to the impurity ionization energy (i.e., $\Delta = e^2/2\varepsilon R$), and, taking into account the fact that $R = a_H$ and $n_m = n_c$, equation (6) turns exactly into equation (1).

In the case of vanadium dioxide, using the values of $R = 1.84$ au $= 0.9$ Å [15] and $\Delta = 0.7$ eV, equation (6) yields $n_{c2} = 0.8 \times 10^{22}$ cm^{-3}. One can see that, indeed, $n_{c2} \gg n_{c1}$ (for VO_2, $n_{c1} \sim n_s \sim 3 \times 10^{18}$ cm^{-3} [9]). On the other hand, the obtained theoretical value of n_{c2} does not coincide exactly with n_m: n_{c2} is a factor of 4 less than n_m, which can be explained merely by the fact that the density n_{c2} corresponds to the commencement of the M→S MIT, and therefore it might be considerably less than the equilibrium density in the metallic phase beyond the transition point. The question of how large is the difference $|n_{c2} - n_m|$ is still to be clarified; here we note only that this value is not very large, even if it 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_2 and SmS are not the best examples in this sense. However, in V_2O_3,[1] 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, 11]. 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_2 [9].

[1] Apropos of V_2O_3, it is pertinent to note that calculations of n_{c1} and n_{c2} for this material would also be of doubtless interest, because the MIT in vanadium sesquioxide is often deemed as a well-known classical example of the Mott transition [1, 10, 16–19]. Most of the data for such calculations are available in the literature: see, e.g., the results on both RF and static ε in the works [16, 17], or those on effective mass in the monograph [10] and some reviews [1]. However, the case of V_2O_3 is more complex than that considered in this paper. The reason for this is that this material is rather an undegenerate semiconductor because of its low transition temperature ($T_t = 150$ K [10] and, consequently, $n_s \sim 10^{15}$ cm^{-3}). This fact makes it impossible to use the simple Thomas–Fermi screening theory, and thus requires a new approach based on a complete modification of all the inferences presented above. In addition, over-screening in strongly correlated electron gas [2] should presumably be taken into consideration. For example, direct calculations from equation (1) would result in a value of $a_H \sim 1$ Å which is obviously underestimated. Provided that $a_H \sim \xi$ (as was shown in [9]), where ξ as before, is the coherence length, this ξ (and hence a_H) should be of order a few nanometres, which has been shown for V_2O_3 recently in the work [18]. Generally speaking, all these problems apparently require some further development, both theoretically and experimentally; particularly, we would like to refer to the work [19] which reports the results of an optical study of the Mott transition in V_2O_3 carried out by time- and frequency-domain spectroscopies in the femtosecond regime.

For samarium monosulfide, taking the values of $\varepsilon_\infty \approx 4$ (the dielectric permittivity of M-SmS at $\omega \sim \omega_p$, the plasma frequency) [20] and $n_m = 1.5 \times 10^{22}$ cm^{-3} [14], we obtain $W \sim 1.8$ eV. Further, the radius of the samarium 4f electron shell is $R = 0.3$ Å and $\Delta = 0.23$ eV (the gap between the 4f-level and the conduction band) [14]. Thus, in the case of SmS, equation (6) yields $n_{c2} = 1.2 \times 10^{21}$ cm^{-3}. Once again, as in the case of VO_2, this n_{c2} is higher than $n_{c1} = 0.8 \times 10^{20}$ cm^{-3} [12, 13] or $n_s = 2 \times 10^{20}$ cm^{-3} [14], but n_{c2} is almost an order of magnitude lower than n_m. Of course, 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 for vanadium dioxide.

We next consider the experiments on photoinduced re-entrant MIT in SmS [8]. The minimum number of the excited electrons $n_{\rm ex}$, required to initiate the M $\rightarrow$ S transition, is $n_{\rm min} = (n_m - n_{c2}) \sim n_m$. The experimental value of $n_{\rm ex}$ can be calculated as:

$$n_{\rm ex} = \frac{(1-r)E}{h\nu d}, \tag{7}$$

where $r = 65\%$ [8, 20] is the reflection of metallic SmS, $E = 0.5$ J cm^{-2} —the laser energy, and $h\nu = 1.6$ eV for $\lambda = 800$ nm—the laser wavelength; $d \sim 200$ nm is the thickness of a layer wherein the absorption occurs for the most part [8]. In equation (7), we do not take into consideration the processes of diffusion and recombination (generally reducing the value of $n_{\rm ex}$) which are apparently negligible for a pulse duration of $\sim$100 fs. Equation (7) yields thus $n_{\rm ex} = 3.4 \times 10^{22}$ cm^{-3}, which is well above the density $n_{\rm min} \sim 1.5 \times 10^{22}$ cm^{-3} indispensable for the transition to occur; that is, the value of E appears to exceed a minimum threshold value. If however the recombination time is comparable to the pulse duration ($\sim 10^{-13}$ s), then equation (7) just gives an overestimated value of $n_{\rm ex}$. Thus, the electronically-induced M$\rightarrow$S transition in SmS has been observed experimentally and, as is shown above, it may be described in terms of the Mott transition.

In view of aforesaid, it would also be interesting to realize the non-equilibrium (i.e. occurring not under pressure) S$\rightarrow$M MIT in samarium monosulfide. However, as far as we know, only one indication on that has been reported in the literature to date (see [12, 13]). The equilibrium pressure-induced MIT in SmS can be described as follows [8, 10, 14]. With an 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 Δ [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 [14]. On the other hand, similarly to the case of VO_2, the MIT in SmS occurs in two stages [9, 13]—first, in the electron subsystem (accompanied by the change of the samarium ion valency $Sm^{2+} \rightarrow Sm^{3+}$), and then in the ion subsystem with the change of the crystal lattice parameter (from 5.97 to 5.70 Å) which is proportional to the valency change [12].

However, as we have seen above, 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 $n = n_{c1}$, 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 under high speed without thermal stress [8]. Such studies, along with the investigation of structural dynamics, would allow elucidation of the physical mechanism of the MIT 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 [1, 3, 4].

For example, the combination of femtosecond optical pump-probe spectroscopy with time-resolved x-ray diffraction has been applied to investigation of the transition in VO_2 [5]. It was shown, among others, 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 [15]. However, this fact does not contradict an electronically-driven transition mechanism [9, 21]. Indeed, the MIT in vanadium dioxide appears to be remarkably complex, and additional experimental efforts are required in order to identify the true origin of the transition, i.e. whether it is primarily caused by the lattice reconstruction or by Coulomb correlations, or whether these mechanisms mutually enhance each other [21]. The latter scenario does seem to be the most realistic, and moreover, it is in accordance with the data of the work [9], where it has been shown that the electron-correlation contribution to the energy gap of VO_2 is $\Delta \sim kT_t \sim 0.1$ eV and the corresponding coherence length is $\xi_1 \sim 15$ Å. The modulation of the electronic spectrum at this point results in distortion of the crystal structure accompanied by formation of the gap $\Delta \sim E_g \sim 1$ eV and by the complete localization of the electrons onto vanadium atoms with the localization radius $R \sim \xi_2 \sim 1$ Å.

Acknowledgments

This research was made possible in part by Award no. PZ-013-02 of CRDF (USA) and the Ministry of Education (Russian Federation). AM gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft under project US 17/3-2. The authors are also indebted to Drs P A Metcalf, V N Andreev, G B Stefanovich and E L Kazakova for helpful discussions.

References

[1] Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1059
Edwards P P, Ramakrishnan T V and Rao C N 1995 *J. Phys. Chem.* **99** 5228
[2] Saarela M, Taipaleenmaki T and Kusmartsev F V 2003 *J. Phys. A: Math. Gen.* **36** 9223
[3] Sundaram S K and Mazur E 2002 *Nature Mater.* **1** 217
[4] Feurer T *et al* 2002 *Phys. Rev.* E **65** 016412
[5] Cavalleri A, Dekorsy Th, Chong H H W, Kieffer J C and Schoenlein R W 2004 *Phys. Rev.* B **70** 161102(R)
[6] Callan J P, Kim A M-T, Roeser C A D and Mazur E 2001 *Phys. Rev.* B **64** 073201
[7] Zeiger H J, Cheng T K, Ippen E P, Vidal J, Dresselhaus G and Dresselhaus M S 1996 *Phys. Rev.* B **54** 105
[8] Kitagawa R, Takebe H and Morinaga K 2003 *Appl. Phys. Lett.* **82** 3641
[9] Pergament A 2003 *J. Phys.: Condens. Matter* **15** 3217
[10] Mott N F 1974 *Metal–Insulator Transitions* (London: Taylor and Francis)
[11] Nagaev E L 1998 *Phys. Solid State* **40** 396
[12] Sharenkova N V, Kaminskii V V, Golubkov A V, Vasil'ev L N and Kamenskaya G A 2005 *Phys. Solid State* **47** 622
[13] Kazanin M M, Kaminskii V V and Solov'ev S M 2000 *Tech. Phys.* **45** 659
[14] Smirnov I A and Oskotsky V S 1978 *Phys.-Usp.* **21** 117
[15] Continenza A, Massidda S and Posternak M 1999 *Phys. Rev.* B **60** 15699
[16] Abe H, Terauchi M, Tanaka M and Shin S 1998 *Japan. J. Appl. Phys.* **37** 584
[17] Jhans H, Honig J M, Chudnovsky F A and Andreev V N 2000 *J. Solid State Chem.* **159** 41
[18] Limelette P, Georges A, Jerome D, Wzietek P, Metcalf P and Honig J M 2003 *Science* **302** 89
[19] Misochko O V, Tani M, Sakai K, Kisoda K, Nakashima S, Andreev V N and Chudnovsky F A 1998 *Phys. Rev.* B **58** 12789
[20] Batlogg B, Kaldis E, Schlegel A and Wachter P 1976 *Phys. Rev.* B **14** 5503
[21] Liebsch A, Ishida H and Bihlmayer G 2005 *Phys. Rev.* B **71** 085109