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Nucleation of metals by strong electric fields

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Recent work on phase transitions in chalcogenides (underlying phase change memory) led to a theory of symmetry-breaking field effects, predicting needle-shaped metallic nuclei and exponentially accelerated nucleation rates. Here, we predict that, in general, any insulator will eventually form metallic inclusions if immersed in a sufficient electric field. These phase transitions are driven, not simply enhanced, by an electric field. Hence, metals can be formed under conditions where they would be otherwise unexpected. This opens the venue of field induced materials synthesis. As a technologically important example, we consider the field driven synthesis of metallic hydrogen at normal pressure. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3703611>]

Phase transitions that are driven by temperature or pressure are everyday occurrences. In this Letter, we describe a concept of insulator-metal phase transitions that are driven by an electric field. That is, even when the metallic phase is otherwise energetically unfavorable, increasing the electric field will eventually cause the transition to occur. The concept was conceived during our recent work¹ on phase change memory where we found that the observations could be consistently explained by a nucleation mechanism that accounts for the symmetry-breaking effects of strong electric fields ($\gtrsim 10^5$ V/cm). Here, we show that the same effect is generally applicable and leads to the prediction that any insulator will at least partially transform into a metal under a sufficient electric field.

That prediction holds regardless of the microscopic mechanism of the insulator to metal transition (densification, crystallization, electron solvation, or others²); it applies equally to solid and liquid states. For example, conductive crystallites will form in insulating glass hosts, and liquid Si (metallic) will form in semiconducting Si. As such, our theory opens the venue of field induced materials synthesis.

A brief survey of relevant phenomena includes the crystallization of chalcogenide alloys under laser beam or applied bias,³ bias induced metal-insulator transitions in vanadium dioxide⁴ (VO₂), and resistive random access memory (RRAM).⁵ Another category is the laser or dc electric field induced crystallization of selected polymorphs in supersaturated solutions, referred to as non-photochemical laser induced nucleation (NPLIN).⁶ The common feature in all of the above is that the electric bias causes the phase transitions to occur exponentially more rapidly than predicted by standard classical nucleation theory (CNT).⁷

We begin our analysis with a brief introduction to the electric field effect in CNT. The free energy of a new particle in the presence of the field is

$$F = A\sigma - \Omega\mu + F_E. \quad (1)$$

Here, A and Ω are the particle surface area and volume, σ is the coefficient of surface tension, and μ is the chemical potential difference between the two phases, taken to be

positive when the bulk new phase is energetically favorable. Eq. (1) does not specify the type of transition. The electrostatic term has the form⁸

$$F_E = -\frac{\varepsilon E^2 \Omega}{8\pi n}, \quad (2)$$

where ε is the electric permittivity of the host insulating phase and the effect of particle geometry is embodied in the depolarizing factor, n . For a sphere, $n = 1/3$, $A = 4\pi R^2$, and $\Omega = 4\pi R^3/3$. In zero field, the maximum of $F(R)$ from Eq. (1) provides the nucleation barrier $W_0 = 16\pi\sigma^3/(3\mu^2)$ and radius $R_0 = 2\sigma/|\mu|$ with typical magnitudes near 1 eV and 1 nm. Maintaining the assumption of spherical geometry, the field reduces the nucleation barrier and radius according to⁷

$$W_{sph} = \frac{W_0}{(1 + E^2/E_0^2)^2} \text{ and } R_{sph} = \frac{R_0}{1 + E^2/E_0^2}, \quad (3)$$

where $E_0 = 2[W_0/(\varepsilon R_0^3)]^{1/2}$ is typically in the range of several MV/cm. The physical meaning of E_0 is that it represents the characteristic field at which the electrostatic energy localized in a sphere of radius R_0 becomes comparable with the classical nucleation barrier W_0 of that particle.

In CNT, μ must be positive in Eq. (1), implying the necessity of a metastable host phase. Another important assumption is that of spherical symmetry. We show next how phase transitions are possible even for the case of energetically unfavorable bulk new phase (negative μ) when a strong electric field is applied and the constraint of spherical shape is relaxed.

In our concept, the free energy of Eq. (1) has two degrees of freedom: spherical symmetry is broken, and when the field is sufficiently strong, needle-like conductive particles aligned with the field become energetically favorable. That can be understood by comparing the electrostatic energy contribution of a sphere to that of a strongly anisotropic prolate spheroid with a large ratio of the major over minor axes, $H/R \gg 1$, for which the depolarizing factor is⁸

$$n = (R/H)^2 [\ln(2H/R) - 1] \equiv (R/H)^2 L. \quad (4)$$

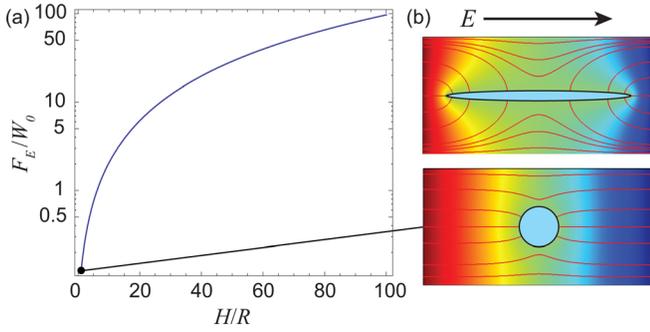


FIG. 1. (a) Absolute, normalized value of the electrostatic energy contribution, F_E/W_0 , to the free energy as a function of nucleus aspect ratio; $H/R=1$ corresponds to a sphere. A value of $E/E_0=0.25$ and nucleus volume of $4\pi R_0^3/3$ were used. (b) Surface plots of the electric potential and streamlines of the electric field illustrate the greater electrostatic energy reducing effect of elongated metallic nuclei versus spheres. An elongated nucleus concentrates the field at its tips, similar to the lightning rod effect, possibly triggering further nucleation events.

Considering particles of equal volume, the electrostatic contribution is greater for a prolate spheroid by a huge factor of approximately $(H/R)^2 \gg 1$ (see Fig. 1). Physically, this enhancement is due to a large induced electric dipole in the needle-shaped particle. Once created, it will act as a lightning rod, concentrating the field and triggering further nucleation.

The exact shape of the elongated nucleus is not known, but modeling with either spheroidal or cylindrical particles leads to differences only in numerical coefficients.¹ We opt for the mathematically concise cylinder shape with height H much greater than its radius R . In that case, $A = 2\pi RH$, $\Omega = \pi R^2 H$, and the free energy is given by,

$$F_{cyl} = \frac{W_0}{2} \left(\frac{3RH}{R_0^2} \pm \frac{3R^2H}{R_0^3} - \frac{E^2 H^3}{E_0^2 R_0^3} \right), \quad (5)$$

with the approximation $n \approx (R/H)^2$ for $H \gg R$ from Eq. (4). As shown in Fig. 2, the free energy landscape exhibits a range of low nucleation barriers at small R .

In the second term of Eq. (5), we allow μ (included in R_0) to be negative for a new phase that is energetically unfavorable in the bulk. In that case, Eq. (5) predicts needle-shaped second phase particles to be energetically favorable provided that

$$\frac{H}{R} > \sqrt{3 \left(1 + \frac{R_0}{R} \right) \frac{E_0}{E}}. \quad (6)$$

Fig. 2 shows, indeed, that in a strong field the system lowers its energy more easily by forming elongated particles, regardless of the sign of μ . That is the general mechanism by which the field can drive the transition.

While post-nucleation growth is beyond the present scope, the final state can be readily described in the same framework. If the final state is a stand-alone metallic body in the same field E , then the obvious modifications to Eqs. (5) and (6) will be as follows: μ will be the chemical potential of the metal, σ its surface tension, and ε should be set to unity, assuming that the body is in vacuum. Therefore, the transformation will result in an entirely metallic, needle-shaped body.

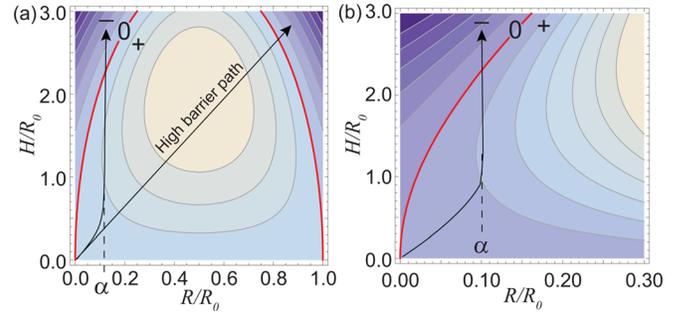


FIG. 2. Free energy landscape of FIMS as a function of nucleus radius, R/R_0 , and height, H/R_0 [from Eq. (5) with $E/E_0=0.25$]. Contour spacings are $F/W_0 \sim 0.1$. Regions of positive and negative free energy are separated by the zero contour (red). In (a), the new phase is stable in the bulk [negative sign in Eq. (5)], while in (b) the new phase would be unstable [positive sign in Eq. (5)] if the electric field were not present (note the difference in scale). The contours show that when the field is strong enough, nucleation pathways with much lower barriers become available for elongated embryos, regardless of bulk phase stability without the field.

Eq. (5) suggests that nuclei with $R \rightarrow 0$ are most favorable. Realistically, R must be greater than some minimum value determined by extraneous requirements, such as sufficient conductivity to support a large dipole energy or mechanical integrity. Based on relevant data, it was estimated¹ that $R_{min} = \alpha R_0$, where $\alpha \sim 0.1$ is a phenomenological parameter. That puts R_{min} in the range of molecular size. The free energy in the region $R < R_{min}$ is substantially larger than described by Eq. (5) because the energy reducing effect of the electric field cannot be manifested by such thin particles; this can be approximated by a potential wall. With the latter in mind, the maximum of the free energy in Eq. (5) (with $R = \alpha R_0$) yields the nucleation barrier¹

$$W_{cyl} = W_0 \frac{\alpha^3/2 E_0}{E}. \quad (7)$$

The associated critical aspect ratio is $H_c/R_{min} = E_0/(E\alpha^{1/2}) \gg 1$.

The barrier of Eq. (7) is suppressed when $E > E_c = \alpha^{3/2} E_0$. Correspondingly, nucleation of needle-shaped particles is vastly accelerated by electric fields under which spherical particle nucleation would be practically unaffected [cf. Eq. (3)], as illustrated in Fig. 3. Moreover, for the case of $\mu < 0$, there exists a field range ($E < E_0$) where spherical nucleation is not possible and nucleation only occurs via needle-shaped embryos (left of the vertical line in Fig. 3).

It should be noted that while significant as the phase change driver, the electric polarization here remains small with respect to the total charge distribution in the needle-shaped embryo. Indeed, the charge moved to the embryo ends is estimated as $q_E \sim EH_c^2$, with H_c given below Eq. (7). That should be compared to the total charge of the embryo $q \sim eH_c R_{min}^2/a^3$, where e is the electron charge and a is the characteristic interatomic distance: $q_E/q \sim E_0/(E_{at}\sqrt{\alpha}) \ll 1$, where $E_{at} \sim e/a^2 \sim 10^9$ V/cm is the characteristic atomic field. A more accurate analysis in Ref. 8 (p. 17) shows that the ratio q_E/q is further reduced by a factor of $1/L$, where $L \gg 1$ is defined in Eq. (4).

Another comment concerns the field induced transitions in the vicinity of a bulk phase transition determined by the

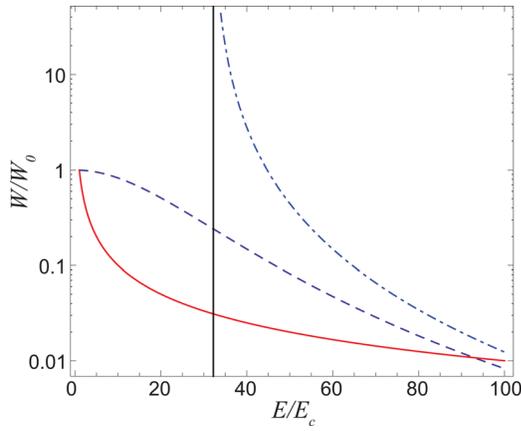


FIG. 3. Normalized nucleation barrier, W/W_0 , as a function of the applied field, E , relative to the critical field E_c . The barrier for nucleation of elongated particles (red, solid line) [Eq. (7)] is compared to that of spheres [Eq. (3)] for the cases of: a stable new phase [$\mu > 0$ in Eq. (1)] (blue, dashed line); and an unstable new phase [$\mu < 0$ in Eq. (1)] (blue, dashed-dotted line). Nucleation of elongated particles is highly favored across the entire field range ($E_c < E < E_c/\alpha^2$), where $\alpha = 0.1$. Nucleation in the region $E > E_c/\alpha^2$ is uncertain due to the requirement of ultra-small nuclei. In the region to the left of the vertical line, the field can drive the transition to a phase that would be unstable without the field.

critical temperature (T_c), pressure, or concentration, such as the bulk phase transition between the insulating and conductive phases of VO_2 at $T_c = 340$ K. Using the standard approximation $\mu = \mu_0(1 - T/T_c)$, where μ_0 is the chemical potential difference between the two phases at zero temperature, results in the corresponding renormalization [cf. Eq. (3)]

$$W_0 \propto (1 - T/T_c)^{-2}, R_0 \propto (1 - T/T_c)^{-1}, E_0 \propto (1 - T/T_c)^{1/2}. \quad (8)$$

Because R_{min} is determined by the microscopic structure and remains practically independent of T , we observe that $\alpha \propto (1 - T/T_c)$. As a result, the barrier W_{cyl} is temperature independent.

The latter conclusion is in striking contrast to the prediction of CNT that the barrier is strongly temperature dependent, $W_0 \propto \mu^{-2} \propto (1 - T/T_c)^{-2}$. Thus, we observe that field induced nucleation becomes exponentially more effective than classical nucleation of spherical particles in the proximity of a bulk phase transition. It can dominate even under relatively weak fields $E > E_{00}\alpha_{00}^{3/2}(1 - T/T_c)^2$, where E_{00} and α_{00} are the zero-temperature values of E_0 and α . This effect can be rather substantial. For example, $1 - T/T_c \approx 0.2$ for the case of VO_2 at room temperature yields $E > 100$ V/cm.

Simply stated, field induced nucleation dominates in the proximity of bulk phase transitions; the required electric fields can be either externally applied, say, in the form of low power laser beam, or generated internally as a result of minute material nonuniformities. We note that needle-shaped nuclei in polycrystalline VO_2 have been observed,⁹ which can be attributed to nucleation induced by the internal fields generated by grain boundaries.

We note, however, that the closeness of the bulk phase transitions in chalcogenide alloys of $\text{Ge}_2\text{Sb}_2\text{Te}_2$ (see, e.g., Ref. 10) and related re-normalizations of Eq. (8) were overlooked in the estimates of Ref. 1. Taking these re-normalizations into account will make the field induced

nucleation rate several orders of magnitude higher, thus much more favorable than estimated in Ref. 1.

Field driven phase transitions would also be enhanced in laser or dc fields that are sufficiently strong to ionize the material. Indeed, that process would generate free charge carriers, thereby increasing the system polarizability and its related trend toward the transformation.

Turning back to the relevant observations, field induced nucleation can explain them, assuming that the product of nucleation is a highly conductive filament. That is well justified for the cases of chalcogenide alloys and RRAM. However, the final products of NPLIN are non-metallic new phase particles. Yet, the very fact that NPLIN is triggered by lasers indicates that the induced polarization can adiabatically follow the optical frequency electric field, which is only possible for metals. Our hypothesis, therefore, is that the above described nucleation barrier suppression takes place for an intermediate phase that is metallic in nature, which finally transforms into the non-metallic crystals observed in the NPLIN experiments. The structure of the intermediate metallic particles remains an open question.

As a provocative example, consider next the synthesis of metallic hydrogen (MH). Predicted by Wigner and Huntington¹¹ in 1935, solid MH has not yet been observed under static pressures of up to 342 GPa.^{12,13} Dynamic compression beyond 200 GPa has also been employed.^{14,15} The only direct evidence thus far was the brief observation¹⁶ of a highly conductive liquid phase under a shockwave pressure of 140 GPa and temperature around 3000 K. We will now attempt a rough estimate of the electric field range under which MH could be synthesized under standard pressure.

We use¹⁷ $\mu \sim 0.1 \text{ Ry}/a_B^3$ for the difference in chemical potential between the molecular and monatomic phases, and $\sigma \sim 1 \text{ Ry}/a_B^2$ (order of magnitude estimate for significantly different structures), where a_B is the Bohr radius. This yields $R_0 \sim 10 \text{ \AA}$ and $W_0 \sim \mu R_0^3 \sim 10^3 \text{ eV}$. Also assuming¹⁴ $\alpha = 0.1$, and $\varepsilon \sim 1$, we obtain the critical field $E_c = \alpha^{3/2}E_0 \sim 10^7 \text{ V/cm}$, or laser intensity $I_c \sim 10^{12} \text{ W/cm}^2$. Therefore, the practical window for field induced synthesis of MH is $10^7 < E \ll 10^9 \text{ V/cm}$. That field range could be decreased in the proximity of the bulk phase transition (e.g., close to the critical pressure).

Investigation could also be conducted with hydrogen rich alloys, such as¹⁸ CH_4 (or other paraffins) or SiH_4 (H_2)₂. We note that while MH particles can be field induced according to our estimates, they will be metastable upon field removal due to the inequality in bulk chemical potentials ($\mu < 0$) and the metastability barrier¹⁹ of $\sim 1 \text{ eV}$.

We shall end by briefly mentioning the possibility of reverse, metal-to-insulator transformations when the electric potential (rather than the electric field) is kept constant. Here, we limit our arguments to the analogy of the well-known elementary problem of a capacitor with plates partially immersed in water. When it is disconnected from the voltage source U , its charge Q (hence, electric induction) is conserved and the energy $Q^2/2C$ tends to decrease via the increase in capacitance C ; this is achieved by pulling in the more polarizable substance (water). That is analogous to creating more polarizable metal particles in the above analysis. However, the capacitor will push water away when it is

connected to the voltage source in order to decrease its energy $CU^2/2$. In terms of our consideration, that corresponds to eliminating the more polarizable metal phase.

In conclusion, we have shown how a symmetry-breaking electric field can drive metal synthesis in any dielectric. The transition is initiated by the nucleation of a needle-shaped particle and eventually results in a uniform, elongated, metallic body. We have determined the conditions under which such phenomena are possible and their corresponding transformation rates. From a practical standpoint, the concept of field induced phase transitions presents a unique pathway for the synthesis of materials that may be otherwise unobtainable.

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