American Journal of Condensed Matter Physics 2013, 3(5): 142-150
DOI: 10.5923/j.ajcmp.20130305.05

Hysteresis of Solid-State Reactions: Its Cause and Manifestations

Yuri Mnyukh

76 Peggy Lane, Farmington, CT, USA

Abstract The aim of this article is to establish the physical origin of hysteresis in solid state reactions. It had not been identified by the conventional science that remained limited by phenomenological modeling. The hysteresis revealed itself in detail as an essential component of the molecular mechanism of phase transitions in our studies of good transparent single crystals by optical microscopy and X-rays. The exclusive cause of hysteresis is *nucleation lags* and rooted in the nature of the nucleation far from the classical "random fluctuation" model. The nuclei are localized on crystal defects where nucleation lags are encoded. The hysteresis in structural, ferromagnetic and ferroelectric phase transitions, and upon magnetization and polarization results from the underlying role of structural rearrangements in these processes. Formation of structural and magnetic hysteresis loops is analyzed in detail.

Keywords Hysteresis, Structural Hysteresis, Magnetic Hysteresis, Ferroelectric Hysteresis, Phase Transition, Range of Transition, Nucleation, Hysteresis Loops, Magnetization

---

1. The Phenomenon of Hysteresis

Hysteresis is a lagging to respond when the system is prompted to change by a control parameter. The phenomenon does not depend on the direction of the change and is not rooted in kinetics. In solid-state reactions we will call it *structural* when it relates to change of crystal structure and *magnetic* when it relates to change of magnetization (or simply *hysteresis of polarization* in relation to electric polarization). The term "hysteresis" in the condensed matter literature is frequently assumed only the magnetic hysteresis.

Hysteresis is a significant feature of phase transitions and other solid-state reactions. The phase transitions caused by change of temperature or pressure, or by application of magnetic or electric field, occur not at the point (T_O if it is temperature) when the equality of free energies of the phases is achieved, but *after* that by a finite value. In technology the phenomenon is found useful in some applications and detrimental in others, but that topic is outside the frames of the present article.

The following questions are critical when dealing with the hysteresis. Are there solid-state reactions without hysteresis? Why it is wide in some cases and narrow in others? Is its magnitude a physical constant for a given phase transition? If observed, can it be reduced? Can it be completely eliminated? If yes, then how? Why and how its notorious loops form, and what are the factors that determine their shape? What is the relation, if any, between the temperature and ferromagnetic (and ferroelectric) hysteresis?

2. Conventional Science: Phenomenological Modeling

Setting aside empirical data and merely opinions, scientifically-founded answers with explanations to the above questions are not, and cannot be, found in the literature. They are hidden in the origin of the hysteresis that has not been identified.

Those who believe in the Landau's theory[1] of second-order phase transitions must also accept that those phase transitions are hysteresis-free. This inference is immaterial, however, since sufficiently documented second-order phase transitions are not found[2,3]. Then hysteresis is a feature of first-order phase transitions only. But is it inevitable in all of them? According to generally held views the transition "may or may not occur" at the temperature T_O when the free energies of the two forms become equal. The actual mechanism of first-order phase transitions[2,4,5], briefly summarized in Section 4, will explain why they were incorrect at that point.

There is no lack of literature on hysteresis. The three-volume (2160 pages) set *The Science of Hysteresis*[6] published in 2007 is an example. All that science was devoted to mathematical descriptions of its manifestations. A more appropriate title would be "The Science of Hysteresis Modeling" due to absence there of anything about the physical nature of the phenomenon. From practical point of

---

* Corresponding author:
yuri@mnyukh.com (Yuri Mnyukh)

view the theoretical modeling of hysteresis is useful. But wouldn't it be better to do it while already understanding its physical origin? Probably some of that modeling would not be even needed.

The fact that the origin of hysteresis was not identified by solid state science does not mean it had not been discovered and publicly revealed. It was done already in 1979 in regard to the structural hysteresis in a special section "Hysteresis of Polymorphic Transitions" in the article *Molecular Mechanism of Polymorphic Transitions*[7]. Not one of the ensuing references to it has been related to the above section. The finding of a *nucleation* as being the exclusive cause of hysteresis is remaining unknown. The purpose of this article is to fill the void. The structural hysteresis in solids is presented here in more detail and in conjunction with the magnetic hysteresis.

3. "What Causes Magnetic Hysteresis?"

Probably, the most known and consequential is the *magnetic hysteresis*. Its cause has not been found by the current theory. Here the hysteresis modeling dominates as well. The regular *International Conferences on Hysteresis and Micromagnetic Modeling* (the 9th was held in 9013) illustrate this fact.

But the sixteen authors of[8] thought it would be beneficial to understand it, pointing out that magnetic hysteresis is fundamental to magnetic storage technologies and a cornerstone to the present information age. They posed a question "What causes magnetic hysteresis?" and stated that all the "beautiful theories of magnetic hysteresis based on random microscopic disorder" failed to explain their own data. Their answer to the above question was: "New advances in our fundamental understanding of magnetic hysteresis are needed".

No such advances are possible without proper understanding of ferromagnetic state and phase transitions first. The insurmountable obstacle to that understanding is the conventional belief that ferromagnetic phase transitions are, according to the common classification, of a "second order", in spite of the fact such phase transitions must not exhibit hysteresis. (As stated by Vonsovskii[9], the theory of second-order phase transitions provided an "impetus" to studies of magnetic phase transitions). The new fundamentals of ferromagnetism and phase transitions [2,10,11] remove that basic contradiction. They demonstrate that the standard *exchange field* theory of ferromagnetism by Heisenberg, assuming existence of additional extremely strong spin interaction, has not been successful and was not even needed. It was replaced by the *crystal field* and a natural assumption that *spin orientation is uniquely bound to its carrier*. It followed at once that ferromagnetic state is *a property* of the crystal structure, that both ferromagnetic phase transitions and magnetization require structural rearrangements. The contribution of the magnetic interaction into the total free energy of a ferromagnetic crystal is relatively small rather than dominant. The magnetic structure (the positional and orientational spatial distribution of the spin carriers and their spins in the crystal lattice) is dictated by the crystal packing, and not, as previously assumed, the other way around.

The mechanism of structural rearrangements in solids is a nucleation and interface propagation[2,4,5,7]. The *structural hysteresis* is one of its manifestations which in case of magnetic crystals is inevitably accompanied by the *magnetic hysteresis*.

It can be seen now that finding the source of magnetic hysteresis was impossible without the new understanding that magnetic phase transitions and magnetization resulted from the crystal-structural rearrangements. The answer to the above question "What causes magnetic hysteresis?" was given in the book[2] six years prior to the time the question was posed. The answer was: *nucleation*. Somehow the sixteen authors of[8] missed it.

4. The Cause of Structural Hysteresis as Seen in Optical Microscope

As to the cause of structural hysteresis, it will be illuminating to recall the experiments performed many years ago[12]. Phase transitions in small (~1 mm) transparent single crystals of *p*-dichlorobenzene (PDB) were investigated by direct observation in optical microscope equipped with a heating/cooling stage. Their temperature T_0 = 30.8℃ when the free energy F of its H (above T_0) and L (below T_0) phases are equal, $F_H(T_0) = F_L(T_0)$, was convenient to do the observations. Every crystal was subjected to a slow heating or/and cooling. Fig. 1 is a photograph of phase transition in one of the heating experiments. Here are some results. Phase transitions start from nucleation *after* the T_0 has been passed. Nucleation is always *heterogeneous*, located at the crystal defects. The actual temperature of phase transitions did not – and could not – coincide with T_0, considering that no reason exists for the transition to go in any direction when $F_H = F_L$. In other words, the temperature T_0, usually called "phase transition temperature" (and sometimes even "critical temperature") is the temperature where phase transitions cannot occur. But the possibility to occur at any other temperatures, except of a small region around T_0, is theoretically unlimited. Heterogeneous nucleation requires a finite energy for activation, which makes *threshold* nucleation lags inevitable. If T_n is the actual temperature of nucleation, the minimum (threshold) overheating in PDB was $\Delta T_n = T_n - T_0 = \sim 1.9$℃. The threshold overcooling was always greater. An assertion by Landau and Lifshitz[1] that overheating or overcooling is *possible* in first-order phase transitions is not applicable to solid-state reactions. There hysteresis is inherently *inevitable*. It can be small, but finite (see Section 8). In general, better crystals exhibit wider *hysteresis*. An extreme case is the observation of melting at 53.2℃ of the PDB crystals still in their L-phase, being "too perfect" to contain even a single suitable defect to serve as a nucleation site of the H-phase. This observation also illustrates absence of a homogeneous nucleation. The hysteresis in PDB crystals was typical for all other investigated objects.

Figure 1. An example of phase transition in a transparent single crystal of *p*-dichlorobenzene. It is a crystal growth of well-shaped single crystal of the new (higher-temperature) phase within the lower-temperature phase. The transition started from a visible crystal defect at $T_n > T_o$ by several degrees. There is no rational crystallographic orientation relationship between the initial and new phases

5. "Non-classical" Peculiarities of Nucleation

Thus, observations of real phase transitions of transparent single crystals bring about essential information on the origin of their hysteresis. *Nucleation* is its exclusive cause. Even more is hidden in the peculiarities of the nucleation[2,5,13]. Only *optimum microcavities* - conglomerations of vacancies, and not any other kind of defects, serve as the nucleation sites. The nucleation is not a random successful fluctuation as usually assumed, *e.g.*[14], it is *predetermined*. Special experiments have revealed that every potential nucleation site contains a "pre-coded" individual temperature of its activation T_n. In the cyclical phase transitions the T_n was the same only as long as the transition was initiated in the same nucleation site. Generally, if the temperature is slowly rising, and there are several potential nucleation sites, the one of lowest temperature T_n would be actually activated. The T_n was different in different crystals. These specific features of nucleation of solid-state reactions provide previously unavailable authentic interpretation of the hysteresis itself and all its manifestations.

6. Range of Transition

The "jumps" of physical properties in phase transitions are never instant. Upon heating or cooling they always spread over a temperature range, narrow or wide, exhibiting a "sigmoid" curve (Fig. 2). It is usual to (erroneously) take the inflection point of the curve as the "transition temperature" or even as the "critical point". Phase transitions over "wide" temperature range are called *diffuse*. The "diffuseness" is not the manifestation of a specific transition mechanism. It results from the non-simultaneous nucleation in different particles, or parts, of the specimen. Any transition in a powder or polycrystalline specimen is "diffuse", the variation being only how much. The width of a transition range is not a fixed value, being a characteristic of the particular crystal imperfection, rather than an inherent property of the substance. For instance, the range of transition will be sharply different for a single crystal and the powder made from it. Concluding, (a) range of transition is a range of *nucleation*, (b) it is affected by the sample condition / preparation, (c) it is located entirely outside T_0 : above it upon heating and below it upon cooling.

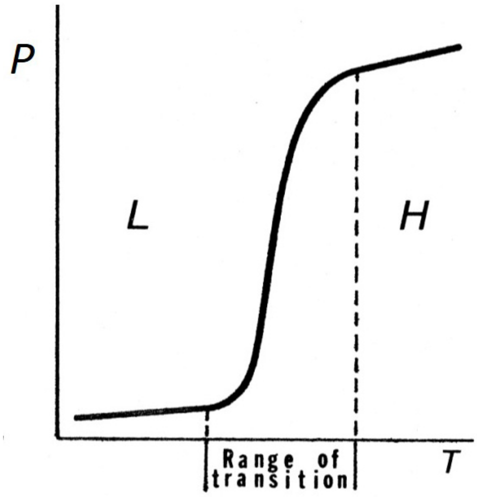


Figure 2. Typical "sigmoid" plot of a physical property *P* upon heating through a phase transition. Its delineation in the temperature range of transition is actually determined by the relative quantities of H- and L-phases in the sample due to non-simultaneous nucleation

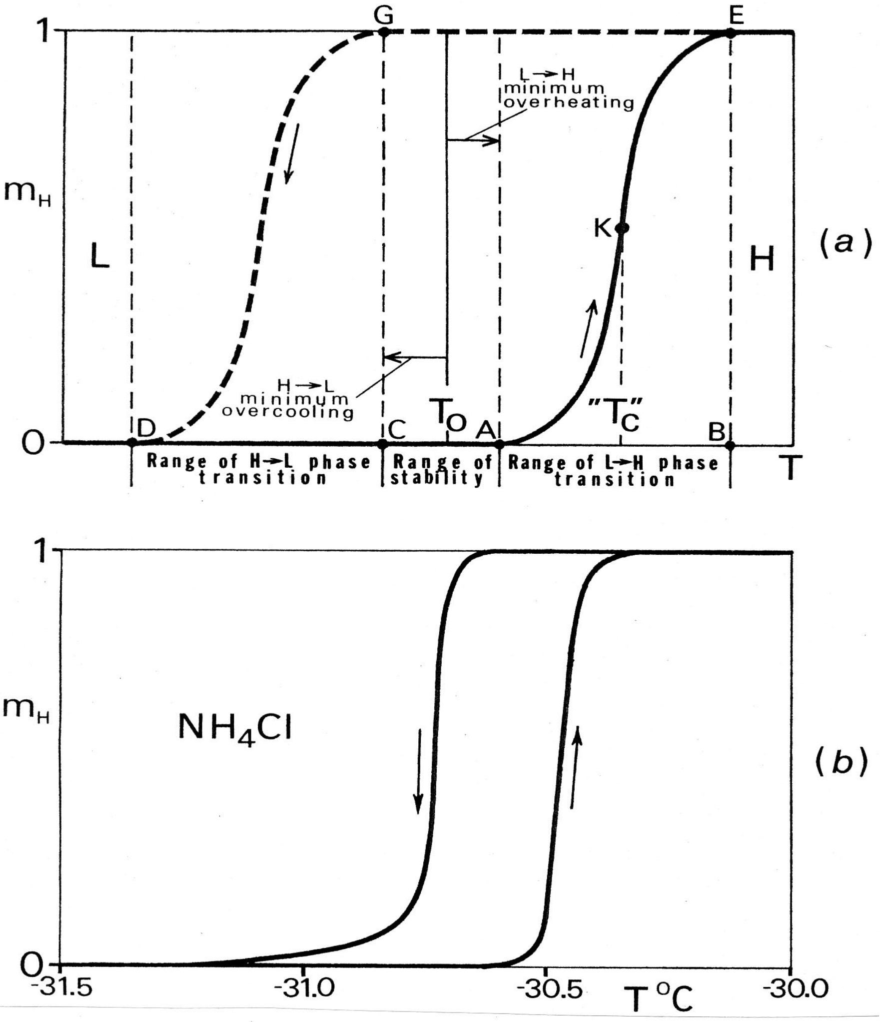
7. Hysteresis Loop of a Phase Transition

The AE and GD curves in Fig. 3 represent mass fraction m_H of the H-phase. The sigmoid curve *P (T)* in Fig. 2 simply delineates the mass ratio of the phases in the two-phase range. In a proper scale it becomes the right part of the hysteresis loop (AE in Fig. 3). Existence of the right part necessarily means that the left part (GD) would be found in the reverse run. It is important to note that the phase transition can be reversed only after *T* is lowered below T_0, and even further to exceed a certain threshold range of stability, to activate an L-nucleus. The hysteresis loop in a small single crystal particle is rectangular. The sigmoid shape of the plots AE and GD is for the systems of many particles. It is indicative of two factors acting in opposite directions as the temperature rises. They are: (1) increase in the number of suitable nucleation sites per unit mass, and (2) decrease of the mass of the original phase. The former factor dominates in the initial stage, and the latter in the final stage of the phase transition.

8. When Hysteresis is Small

There are circumstances when hysteresis in solid-state phase transitions (and any other structural rearrangements in solids for that matter) can be especially small. Two such cases will be outlined here, but they are presented in greater detail in[2 (Sec. 2.8 and 2.9.3.3)], as well as in[5,7,16].

One case is nucleation in layered crystals A layered structure has strongly bounded, energetically advantageous two-dimensional (2-D) units − molecular layers, while the interlayer interaction is weak. Change from one polymorph to the other mainly involves the mode of layer stacking. Real layered crystals always have numerous defects resulted from imprecise layer stacking. Most of these defects are minute microcavities in the form of wedge-like interlayer cracks concentrated at the crystal faces. In such a microcavity there is always a point where the gap has the optimum width for nucleation. There the molecular relocation from one side of interface to the other occurs with no steric hindrance and, at the same time, with the aid of attraction from the opposite wall. In view of a close structural similarity of the layers in the two polymorphs, this nucleation is *epitaxial*. There is a simple answer to why the temperature hysteresis ΔT_n in *epitaxial* phase transitions is small. Due to the abundance of wedge-like microcracks, there is no shortage in the nucleation sites; at that, the presence of a substrate of almost identical surface structure acts like a "seed". As a result, only small overheating or overcooling is required to initiate phase transition. Without a scrupulous verification, these phase transitions may seem "instantaneous", "without a hysteresis", “cooperative", "displacive", "second-order", *etc*., but they are still a nucleation-and-growth.



(a) (Schematic) "Sigmoid" curves AE and GD, each representing m_H in the heterophase (L+H) temperature range of transition. Together they form a hysteresis loop DAEGD. Range of stability CA consists of two threshold lags too small to activate nucleation within. The inflection point K is not a "critical point" (or "Curie point"). It marks the temperature of the maximum number of activated nucleation sites;

(b) (Experimental) The hysteresis loop in NH_4Cl (Dinichert[15])

Figure 3. Hysteresis loop of a solid-state phase transition (m_H is mass fraction of H phase)

Besides the hysteresis caused by formation of a 3-D nucleus to initiate the structural rearrangement, there is another type of hysteresis, much smaller, related to propagation of the immerged interfaces. It has been shown that its advancement in the normal direction also requires some overheating/overcooling. This hysteresis involves a 2-D nucleation. The 2-D nuclei form heterogeneously as well, but there is a significant difference in their function. While only a single 3-D nucleus at an *optimum microcavity* is needed to start a transition, a sufficient concentration of appropriate defects is required to keep the interface moving. These defects are also microcavities, but smaller, although not just individual vacancies. They were named *vacancy aggregations.* One such 2-D defect acts as a nucleus in reformation of a single molecular layer of the crystal and disappears when it is completed. Then another 2-D defect is needed to build next layer.

Existence of two kinds of nucleation − and the associated two-level hysteresis − means that a phase transition, ones started by a 3-D nucleus, may continue at a lower overheating/overcooling, provided the temperature is kept outside the 2-D nucleation threshold.

Another consequence relates to the exact value of T_0. It is not enough to find it as the temperature when the interface does not move in any direction. The two phases are not in dynamic equilibrium at their interface. The T_0 can be determined only approximately as being within the temperature range consisting of the positive and negative 2-D nucleation threshold lags.

9. Magnetization and Its Hysteresis

In the following we will use term *magnetization* towards any change in the magnetic state of a material. We start with two statements.

(1) Definition: "A phase, in the solid state, is characterized by its structure. A solid-state *phase transition* is therefore a transition involving a change of structure, which can be specified in geometrical terms" (Megaw,[17]).

(2) Orientation of a spin in the magnetic material is uniquely bound to the orientation of its atomic carrier[2 (Chapter 4)] and[10,18].

Let us assume a phase diagram where the free energy F of a ferromagnetic material is presented in coordinates of the control parameters T (temperature), H (applied magnetic field), and others. Application of any one will move F over the diagram and can cause it to intersect a border between the areas of the phase stability, giving rise to a phase transition − a *structural* phase transition in accordance with the Statement 1,. The molecular mechanism of the phase transition does not depend of which control parameter affected F value; the mechanism will be the same, namely, a change of the crystal structure by nucleation and growth. That will bring about a change in the spatial positions and orientations of the spin carriers and their spins as well. In other words, ferromagnetic phase transition is *accompanied by magnetization*. The hysteresis of that structural rearrangement, caused by nucleation, will be *accompanied by magnetization hysteresis.*

Magnetization not necessarily related to phase transitions: it takes place every time magnetic field is applied to a ferromagnetic. There is a certain difference in how the control parameters T and H act on a ferromagnetic crystal. Temperature T is a scalar. It is responsible for the level of thermal vibrations of all constituting particles and thus affecting their mutual bonding. The applied field H, on the other hand, is a vector acting only on the spin carriers over the direction of their spins (see Statement 2). Considering that magnetic interaction constitutes only small part of the crystal free energy[2 (Chapter 4)] and[18], it can be said qualitatively that H is a relatively weak control parameter. If the directions of H and spins differ, a readjustment can occur to lower F by making spins coincide with, or be closer to the H direction. This is a *magnetization* not involving phase transition. Finding how it materializes is a high priority issue *per se* and the key to explanation of magnetic hysteresis.

The conventional accounts for the magnetization is vague[19]. It is usually described, without going into details, as a "domain rotation". No attempts are made to theoretically justify the experimental fact that magnetization is realized, at least in most cases, by moving interfaces. The second way of magnetization − by spin rotation in the original crystal structure remaining intact − is believed to also exist.

The new fundamentals of ferromagnetism[2,18] account for the magnetization and its hysteresis in a straightforward and coherent way by simply accepting that orientation of a spin is bound to its atomic carrier (Statement 2 above). It follows immediately that *magnetization* (spin turning) can be realized only by turning the spin carriers. The only way it can be accomplished in a crystal is its complete reconstruction by nucleation and interface propagation. While it is not a phase transition, it is realized like phase transitions do - by nucleation and growth, revealing the generality of nature processes.

Conclusions: (a) Magnetization by applied magnetic field is realized by the nucleation-and-growth structural rearrangement, (b) Any spin reorientation results from a reconstruction of the whole crystal itself, producing the new crystal structure identical to the initial, but in the new spatial orientation, (c) The alternative magnetization mechanism, assuming spin rotation *in* the crystal structure, cannot exist, and (d) *The answer to "What causes magnetic hysteresis?" is: the nucleation lags of the underlying structural rearrangement.*

Now we will limit the term "magnetization" to only designate the process not involving phase transition. It is accepted as an experimental fact that motion of domain boundaries is the main mechanism of magnetization, and that the hysteresis is lags in that motion and lags in formation of new domains. But the question why magnetization is localized on the domain boundaries has not been raised. The cause of the lags has not been identified. Besides, it is erroneously accepted that magnetization can also occur by "rotation" without motion of the domain boundaries. A possible relationship between the magnetic hysteresis loops $M = f(H)$ and the "structural" ones $P = f(T)$ in solid-state phase transitions (Fig. 2 and 3) has not attracted due attention. These failures were rooted in the interpretation of the lags as those of a *magnetic rearrangement in the crystal structure*, rather than a *rearrangement of the crystal structure* itself.

10. Rectangular Hysteresis Loop of Magnetization

Hysteresis loops of magnetization M in external alternating magnetic fields H are a prominent feature of ferromagnetic materials. When analyzing them, one has to take into account whether

- the sample is a single (single-domain) crystal, polydomain crystal or polycrystal,
- the magnetic field H is applied in the "easy" or any other direction,
- the H strength is sufficient to magnetize the sample to saturation,
- the loop is quasi-stationary, or not because it was recorded in a high frequency alternating field.

The actual shape of the hysteresis loops varies depending on these conditions, but, like their phase transition counterparts, they can be entirely accounted for in terms of the structural categories of nucleation and growth.

In the classical experiments by Sixtus and Tonks (S & T), described in a number of sources ([*e. g.*,[9,19]), the experimental arrangement allowed to investigate a magnetic hysteresis loop free of complicating side effects. There the sample - ferromagnetic wire - was turned to a single crystal magnetized to saturation M_S, while the magnetostriction effects and internal strains were eliminated. As a result, the sample exhibited a rectangular hysteresis loop as in Fig. 4. Reducing H' to zero and even applying negative field $H'' < H_n$, where H_n is the magnetic field necessary to start remagnetization, does not affect the $M = M_S$ value. The line A-B is horizontal. An additional applied negative field ΔH, so that $|H'' + \Delta H| > H_n$ would trigger formation of a nucleus with 180^o-reversed magnetization, followed by the fast propagation of a domain interface over the whole sample. The line BC is vertical. Speed of the interface propagation was measured by different authors; it varied depending on the sample and on the strength of the magnetic field. The maximum speed was well below of what can be expected from a "magnetization wave". The magnetic field H_n needed to create the nucleus was called "starting field" ("nucleation field" would be a better name). A somewhat weaker field, called "critical field", was sufficient to keep the interface moving.

Setting aside the shortcomings of the interpretation of the S & T experiments in[18], we will look at the subject in terms of the structural nucleation-growth concept. Remagnetization is not just a "wave of magnetization reversal": change in the M_S direction occurs by the rearrangement of crystal structure at the interface. One may argue that the crystal structures on sides of the domain interface are the same and, by definition, are not different phases. This argument is valid when the variable affecting the crystal free energy is a scalar, such as temperature or pressure, but magnetic field H is a vector. The free energies of two structurally identical domains differently oriented in the magnetic field are not the same, which is the driving force of structural rearrangement at the domain interfaces.

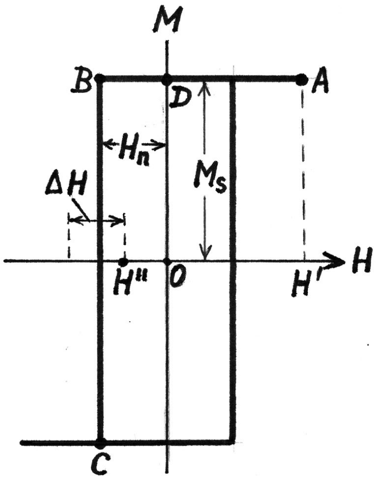


Figure 4. Ferromagnetic rectangular hysteresis loop. See text for symbols and description

The next point to clarify is the reason why M_S, achieved at the strongest positive magnetic field H', remains unchanged after H' is reduced to zero and even farther into the negative side (horizontal line A-D-B in Fig.4). The crystal structure is stable over the region A-D, indeed. In the region D-B, on the contrary, the sample is in the unstable state, since the direction of its magnetization is opposite to H. It remains quasi-stable simply because no structural change can occur without nucleation, i.e., until the negative field is sufficiently strong to increase the instability to the point when a structural nucleus of the opposite magnetization appears. This "starting field" H_n has the same function as the overheating / overcooling in initiating temperature phase transitions. Considering that the H_n value is "pre-coded" in a structural defect, it is not exactly reproducible in different samples. This behavior is no different from the temperature solid-state phase transitions: an energetically unstable phase remains quasi-stable until conditions for the formation of a 3-D nucleus are provided.

Since the domain interface motion was regarded in literature a “wave of magnetization reversal", there was a problem to explain why speed of this wave is too low. What really takes place at the domain interfaces is not a "wave", but a structural rearrangement. Structural phase transitions provide answer to the questions of why some excessive magnetic field ("critical field"), lower than a "starting field", is still required to keep the domain interface moving. The molecular mechanism of structural rearrangement at the domain interfaces is the same as in the structural phase transitions described above. It involves 3-D nucleation to start and 2-D nucleation to continue the process of magnetization. More detailed description of the domain boundaries and the structural rearrangement at them can be found in[2 (Sec. 4.9]. The nucleation lags of that structural rearrangement are the cause of the ferromagnetic and ferroelectric hysteresis loops.

11. Typical Hysteresis Loop of Magnetization

The rectangular hysteresis loop (Fig. 4) is at the basis of all ferromagnetic hysteresis loops. Only nucleation and growth are involved in its formation. The conditions for the rectangular loop to form are: a single-domain crystal, elimination of the magnetostriction adverse effect, a sufficiently strong magnetic field applied parallel/ antiparallel to the direction of spontaneous magnetization, quasi-stationary recording. The shape of a typical quasi-stationary ferromagnetic hysteresis loops, like in Fig. 5 (only its upper part is shown), always deviates from being rectangular to one or another degree. The overall cause for the "typical" loop to not be a rectangular is, evidently, that at least some of those conditions are not satisfied. As a rule, sufficient relevant information does not accompany real hysteresis loops, if at all. These loops are usually related to polycrystals, the fact being given little or no attention, much less properly taken into account.

Not infrequently the illustrative hysteresis loops look like the one in Fig. 6. They have such shape when being not quasi-stationary due to recording in fast alternating fields, instead of recording slowly or by point-by-point. If the applied field *H* changes too fast, the domain interfaces do not have enough time to reach their quasi-stable positions corresponding to the *H* amplitude. The shape of such loop depends on the frequency of the alternating field. Besides, the relaxation time of the internal strains caused by the magnetostriction is too short and is a function of the frequency as well.

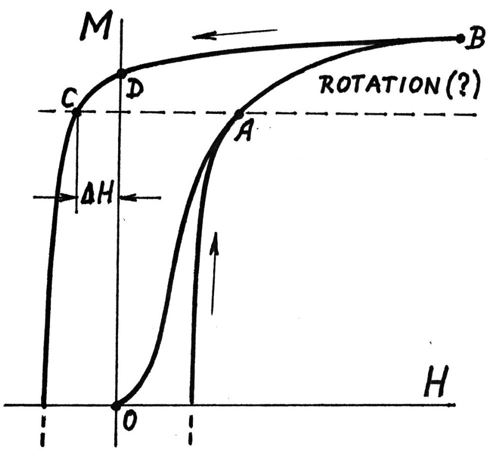


Figure 5. A typical remagnetization hysteresis loop (its lower part is omitted). See text for explanation of its particulars. Its part over the dotted line was erroneously claimed to be due to spin rotation in the structure

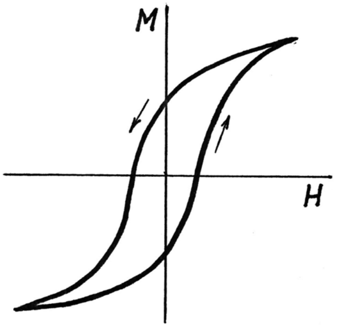


Figure 6. The type of a ferromagnetic hysteresis loop frequently used to illustrate the phenomenon. Such loops are not quasi-stationary and therefore do not fit for analyzing their shape

Only quasi-stationary loops are fit to be analyzed. Their detailed analysis[2, (Sec. 4.13.3)] goes beyond the scope of this article. In brief, their conventional interpretation (Bozorth[19]) was inadequate. A major issue is whether magnetization can occur by a "domain rotation". This magnetization process is claimed to take place in the part of loop marked "rotation (?)" in Fig. 5. According to Bozorth, at point A the magnetization stage owing to motion of the domain boundaries is completed; the magnetic moments of all domains in the sample became uniformly aligned (magnetically saturated) in the "easy" direction of the crystal; farther magnetization in the *H* direction (from A to B) proceeds by a "reversible rotation" of the magnetic moments from the "easy" direction into the direction of the applied magnetic field *H*. It cannot be so, however. The polycrystalline material was treated as if it was a polydomain "single" crystal. Even more indicative is that the alleged rotation of M_S from the "easy" direction by the magnetic field can only be elastic, because the crystal forces will try to return M_S to the "easy" direction. In other words, magnetization by "rotation" has to be reversible, and Bozorth called it as such. But the actual process is not reversible, as evident from the fact that the B → C does not follow B → A. There are a number of reasonable causes, discussed in[2], to account for the ascending M from A to B. Impossibility of spin rotation in a crystal lattice is a major point of the new fundamentals of ferromagnetism and rooted in the fact that spin directions are fixed in their particles and therefore fixed in the crystal structure (see Section 9).

The magnetization B → D shows that a major portion of the structural rearrangements that occurred on the way from A to B is retained, but there is some regression causing the ensuing slope. Whichever processes led to the magnetization A → B, it was accompanied by accumulation of internal strains opposing this magnetization. A subsequent decrease in the *H* strength allows strains to relax by means of structural readjustments at the expense of the magnetization. The strains can be eliminated by annealing the sample under the conditions marked by point B. In this way the curve B → D → C can be flattened, even made horizontal. The moderate *M* decline over B → D → C is not a remagnetization yet. It begins only after *H* changes its sign to the opposite and exceeds a certain threshold -ΔH to initiate nucleation of the oppositely oriented domains. But the sample is still polycrystalline and, contrary to a rectangular loop where a single nucleation act caused a propagation of the domain interface over the whole sample, this time one nucleation act affects only one crystal grain. The "starting fields" H_n are different in different grains. The process would not proceed without $|H|$ increases. Still, this is the most effective magnetization phase $|dM/dH|$ = max, ending at the point equivalent to point A.

A common misconception should be dispelled regarding the role of crystal defects in a magnetization process and formation of hysteresis loops. The defects were always considered only as an obstacle to the motion of domain boundaries. In fact, their role is twofold. In a defect-free crystal neither motion, nor even formation of the boundary is possible. We can imagine a ferromagnet exhibiting a very high coercive force because its crystal structure is "too perfect". Indeed, the shortage of adequate defects for nucleation in very small ferromagnetic particles requires very strong fields for their remagnetization. On the other hand, different kinds of crystal defects that are not suitable to serve as heterogeneous nucleation sites may hamper propagation of domain boundaries.

12. Ferroelectric Hysteresis and Hysteresis Loops

Almost the entire description of ferromagnetic hysteresis and hysteresis loops is directly applicable to the ferroelectric hysteresis and its loops of repolarization in electric fields E. Only two points should be noted.

The *orientational* polarization (*i. e.*, by "rotation") is not possible as well. The difference is that here it is self-evident. The orientation of the electric dipoles in polar dielectrics is an element of their crystal structure. Reorientation of the dipoles in a ferroelectric crystal can occur only by rearrangements of crystal structure at the domain interfaces. Ferroelectrics can be polarized to saturation P_S only in the direction determined by the crystal structure, and not in the arbitrarily chosen direction of the applied field E. Achieving P_S in polycrystalline ferroelectrics in any E direction is conceivable only through growth of the grains that happened to be polarized in the E direction.

Another feature is the *induced polarization*. While spontaneous magnetization M_S by itself does not appreciably depend on H, a spontaneous polarization P_S depends on E to some extent. It is due to the fact that the two electric charges of a ferroelectric dipole are spatially separated in the crystal unit cell. The induced polarization adds to the polarization caused by the structural domain rearrangements and is noticeably present in the hysteresis loops. Specifically, the saturation polarization $P_S(E)$ continues to grow even after all the dipoles are parallel. The induced polarization is strictly reversible and has therefore nothing to do with hysteresis, even though it somewhat affects the hysteresis loop shape. For example, a ferroelectric hysteresis loop cannot be quite rectangular.

13. Conclusions

The cause of hysteresis in solid-state reactions, not previously identified, was experimentally established. The key method of the investigation was optical microscopy of phase transitions in good transparent single crystals. The exclusive cause of the hysteresis is found to be *nucleation lags* due to the features of the nucleation quite different from the classical "random fluctuation" model. The nuclei are located in specific crystal defects - microcavities whose size and shape determine the lags values. The hysteresis in magnetic and ferroelectric materials results from the underlying structural changes. The acquired information on the hysteresis cause and features was applied to interpretation of structural and magnetic hysteresis loops.

REFERENCES

[1] L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Addison-Wesley (1969).

[2] Y. Mnyukh, *Fundamentals of Solid-State Phase Transitions, Ferromagnetism and Ferroelectricity*, Authorhouse, 2001[or 2nd (2010) Edition].

[3] Y. Mnyukh, Second-order phase transitions, L. Landau and his successors, Am. J. Cond. Mat. Phys. 2013, 3(2): 25-30.

[4] Y. Mnyukh, N.A. Panfilova, Polymorphic transitions in molecular crystals - 2. Mechanism of molecular rearrangement at 'contact' interface, J. Phys. Chem. Solids 34 (1973) 159-170.

[5] Y. Mnyukh, Mechanism and kinetics of phase transitions and other reactions in solids, Am. J. Cond. Mat. Phys. 2013, 3(4): 89-103.

[6] *The Science of Hysteresis: 3-volume set,* Ed. G. Bertotti and I Meyergoyz, Academic Press, 2006.

[7] Y. Mnyukh, Molecular mechanism of polymorphic transitions, Mol. Cryst. Liq. Cryst. 52 (1979) 163-200.

[8] M. S. Pierce, C. R. Buechler, L. B. Sorensen, S. D. Kevan, E. A. Jagla, J. M. Deutsch, T. Mai, O. Narayan, J. E. Davies, K. Liu, G. T. Zimanyi, H. G. Katzgraber, O. Hellwig, E. E. Fullerton, P. Fischer, and J. B. Kortright, Phys. Rev. B 75, 144406 (2007).

[9] S. V. Vonsovskii, Magnetism, vol. 2, Wiley (1974).

[10] Y. Mnyukh, The physics of magnetization, arxiv.org /abs/1101.1249.

[11] Y. Mnyukh, Ferromagnetic state and phase transitions, Am. J. Cond. Mat. Phys. 2012, 2(5): 109-115.

[12] A. I. Kitaigorodskii, Y. Mnyukh, Y. Asadov, 1965, Relationships for single crystal growth during polymorphic transformation, J. Phys. Chem. Solids, 26, 463-472.

[13] Y. Mnyukh, 1976, Polymorphic transitions in crystals: nucleation, J. Crystal Growth, 32, 371-377.

[14] K.C. Russell, Nucleation in Solids, in *Nucleation III*, Ed. A.C. Zettlemoyer, M. Dekker (1977).

[15] P. Dinichert, Helv. Phys. Acta 15 (1942) 462-475.

[16] Y. Mnyukh, N. A. Panfilova, N. N. Petropavlov, N. S. Uchvatova, 1975, Polymorphic transitions in molecular crystals - 3, J. Phys. Chem. Solids, 36, 127-144.

[17] H.D. Megaw, Crystal Structures: A Working Approach, Saunders Co. (1973).

[18] Y. Mnyukh, Ferromagnetic state and phase transitions, Am. J. Cond. Mat. Phys., 2012, 2(5): 109-115.

[19] R.M. Bozorth, *Ferromagnetism*, Van Nostrand (1951).