On Cooperative Phenomena

F. Zwicky, *Norman Bridge Laboratory, California Institute of Technology, Pasadena*
(Received December 23, 1932)

The study is proposed of a group of phenomena so far not systematically treated. The term cooperative phenomena is adopted because of the fact that these phenomena are caused by interactions of a great number of elementary particles such as electrons, atoms, etc. These interactions extend over distances which are enormously greater than the usual action radii of the elementary particles. A brief survey of some possible cooperative phenomena in static and in stationary systems is given and their importance in physics, astrophysics, and biology is pointed out. Incidentally a *generalization* of *thermodynamics* from static systems to stationary systems is discussed. The view is advanced that the existence of crystals is due to certain cooperative phenomena which fact would in general necessitate the existence of a *secondary structure of crystals*. The various general contentions and conclusions of this paper are illustrated and applied in the case of *ferromagnetism*.

§1. INTRODUCTION

A CRUDE survey shows that some of the major problems of modern physics may be roughly classified into four groups. These are: (1) The problem of the nuclei of atoms and the existence of elementary particles such as the proton, the electron and the photon; (2) the problem of the interaction of the electromagnetic and the gravitational fields with matter and the problem of unifying the fields; (3) the problem of the universe as a whole; (4) the problem of *cooperative actions* of a great number of elementary particles, and, in particular, the *problem of the solid state*.

The first three problems will probably necessitate radical changes of our current notions about time, space, causality, fields, etc. The fourth problem is of an entirely different nature inasmuch as it seems that no fundamentally new laws must be invented for its solution. The difficulty rather lies in our present inability to visualize the simultaneous cooperation of a great number of particles and the lack of mathematical methods to obtain exact solutions for sufficiently general cases of interactions between many elementary particles.

§2. GENERAL TYPES OF COOPERATIVE PHENOMENA IN STATIC SYSTEMS

I do not make any claim to give a complete list of all possible cooperative phenomena with the following enumeration. The purpose of this investigation rather is to point out a few characteristic examples and to indicate what rôle they actually play or eventually might play in our attempt to comprehend in a scientific way the phenomena around us.

A. Cooperative phenomena caused by the special laws of force which govern the interaction between elementary individual particles

The special group of phenomena which is discussed in this section is closely related to the problem of the existence of equations of state in the thermodynamic sense. It is indeed well known that not every homogeneous physical system which is in thermal equilibrium allows of an equation of state. For example, for a space charge of equally charged particles there exists no universal relation between the pressure, the density and the temperature at a given point.

In order to formulate the conditions which are necessary to insure the existence of an equation of state we first must define what an equation of state is. In thermodynamics we distinguish between *extensive* and *intensive* quantities. Intensive quantities may be obtained by measurements in the immediate neighborhood of the point for which they shall be determined. Density, pressure, temperature, etc., are intensive properties. The value of an extensive property, on the other hand, can be determined only by measurements on the whole system. *An equation of state is a relation between intensive properties exclusively.* No

such relation exists, rigorously speaking, for any real system. We must, however, consider the following approximation. If S is the surface of our system, V its total volume and d a length of the order of the size of a molecule we usually neglect terms of the order Sd/V compared with one. Within this approximation many equations of state exist.

Suppose now that the system which we consider is built up of particles whose mutual energy $\Phi(r, \psi, \vartheta)$ as a function of the mutual distance r and polar angles ψ and ϑ is given by

$$\Phi(r, \psi, \vartheta) = a_0(\psi, \vartheta)r^{-p} + a_1(\psi, \vartheta)r^{-(p+1)} + \cdots. \quad (1)$$

The total potential energy ϵ_P of a particle in our system will be

$$\epsilon_P = \int \Phi(r, \psi, \vartheta)r^2 \sin \vartheta d\psi d\vartheta dr. \quad (2)$$

The integration must be extended over the whole system Σ. Carrying out the integrals over ψ and ϑ we obtain

$$\epsilon_P = A_0 \int dr/r^{p-2} + A_1 \int dr/r^{p-1} + \cdots. \quad (3)$$

From this equation it is evident that $p=3$ represents a critical value inasmuch as the first *integral converges* for an infinitely expanded system only if

$$p > 3. \quad (4)$$

It may of course happen that A_0 or some of the other coefficients are zero, which case will be discussed later. For $p < 3$ the contribution of all particles in a shell between r and $r+dr$ to ϵ_P increases with r. In this case the energy ϵ_P depends very much on the boundaries of our system and no equation of state can exist. For $p > 3$ an equation of state as we have defined it exists.

From these considerations it follows that for $p > 3$ the *individual actions* between neighboring particles play the most important rôle whereas for $p < 3$ we may say that the *cooperative actions between all the particles* are essential for the final equilibrium of the system.

The special group of cooperative actions discussed here is related to the fact that there are important cases with potential energy functions (1) for which

$$p \leq 3. \quad (5)$$

As mentioned already, a system made up of charges e_i of one sign only, that is an electron cloud or an ion cloud, is a system belonging to this class. We have here

$$\Phi_{ik}(r) = e_i e_k/r_{ik} \quad \text{with} \quad p=1. \quad (6)$$

It is well known that no equation of state exists in this case. The pressure in a given point depends not only on the density and the temperature at this point but is greatly influenced by the boundary conditions.

It is also known that for an assembly of electrons the quantum theory postulates an *exclusion principle*. No two electrons in the system may have identical sets of quantum numbers. This means in other words that every electron of the system "knows" what every other electron is doing. This is equivalent to some kind of cooperative action between all the electrons of the system. Whether and how this action is related to the one mentioned above, which is due to $p=1$ is as yet unknown. It is certain, however, that these two cooperative actions play a great rôle for our understanding of the structure of matter.

There is another very important case for which $p=1$. Indeed according to the theory of relativity the structure of the universe as a whole is essentially determined by the gravitational interaction of all the matter which it contains. Again no equation of state can exist, a fact which in many respects complicates the problem of the universe as a whole very much.

It is well known in astrophysics that if gravitation is involved the entropy of an adiabatically closed system does not necessarily increase but may decrease in course of time. Take for instance the case of two big spheres of a monoatomic gas (Emden spheres) which are initially at two different temperatures T_1 and T_2. The sphere S_1 at the higher temperature T_1 radiates energy to the sphere S_2 of the lower temperature T_2. S_2 expands and T_2 is lowered in spite of the absorption of energy. On the other hand, T_1 increases because of the resulting contraction of S_1. This illustrates that if cooperative phenomena are involved ordinary thermodynamics may not be applicable.

A system which is built up of neutral elementary particles usually possesses an equation of state if the gravitational interactions may be

neglected. Indeed the next possible term in the expansion (1) is characterized by $p=3$. This term corresponds to the interaction of two dipoles μ. If we consider the dependency on r alone it is

$$\Phi(r) \propto \mu^2/r^3. \tag{7}$$

At the absolute zero point of temperature this would produce, according to (2), a potential energy ϵ_P per dipole which is proportional to $\log D$, if D is of the order of the linear dimensions of our system. In general, however, the temperature agitation makes two sufficiently distant dipoles practically rotate at random with respect to each other which causes ϵ_P to decrease rapidly enough with the distance to guarantee the existence of an equation of state. This happens for instance in a so-called dipole gas which possesses an equation of state. It also may happen that a particular line-up of the dipoles in space is characterized by a coefficient A_0 equal to zero. In this case the *integral* (2) *is conditionally convergent* and an equation of state may exist because of certain particular circumstances which are related to the formation of a so-called secondary structure. This will be elaborated upon later.

B. Cooperative phenomena which are produced by self-perpetuating electric or magnetic fields

The type of phenomenon which belongs in this group is best illustrated by the following simple example. In a uniformly electrically polarized isotropic medium which has the shape of a long needle the polarization P sets up a so-called Lorentz field $L=4\pi P/3$. If the dielectric constant of the medium is great enough, L may cause the *electric moment* P to be *self-perpetuating*. This polarization causes either the atoms to be stripped of their electrons[1] or it may produce permanent electric moments.[2] The internal field which is set up depends very much on the shape of the medium and the *integral* (2) *is conditionally convergent*. For the center of a cube the field is exactly zero. Both these values, namely $4\pi P/3$ for the needle and zero for the cube are independent of the thickness of the needle and the size of the cube as long as we do not approach

atomic dimensions. This size may, for instance, be infinitely great from which possibility we conclude that the essential characteristics of this group of cooperative actions is that the Lorentz field or some similar quantity is determined by a conditionally convergent sum or a conditionally convergent integral. It depends indeed on the shape in which we let our medium extend to infinite dimensions. The term infinite means here, infinite with respect to the size of the atoms, or infinite relative to the lattice constant of a crystal, etc.

The fields which are set up in ferromagnetic substances belong also to this group. Still other possibilities of self-perpetuating cooperative actions are imaginable, although they are not in common use in physics.

C. Other cooperative phenomena

I again give an example for illustration. It was first proposed by U. Dehlinger[3] in his theory of recrystallization. Dehlinger investigated the relative equilibrium of two parallel chains of atoms whose individual interactions are given. He shows that two dynamically stable configurations are possible. One is characterized by a constant and for both chains equal spacing of the atoms along the chain. There is another stable configuration, however, which is characterized by unequal spacings. In this arrangement there occur periodically slight accumulations, and slight scarcities, of atoms along the chain. Dehlinger calls them "Verhakungen." Under ordinary circumstances an individual "Verhakung" is unstable. A row of Verhakungen following one another in sufficiently short intervals, however, results in a dynamically stable configuration. The mutual stabilizing action of a row of Verhakungen is evidently a cooperative phenomenon which depends on the interaction of many atoms.

In two or three-dimensional arrays of atoms conditions are far more complex. From the fact that crystal lattices show many dynamically stable but thermally pseudostable configurations it must be inferred that arrangements similar to a row of Verhakungen are very frequent.

Another case of a cooperative phenomenon according to the quantum theory is related to the energy content of a solid body. This energy

[1] K. F. Herzfeld, Phys. Rev. **29**, 701 (1926).

[2] F. Zwicky, Phys. Rev. **38**, 1772 (1931).

[3] U. Dehlinger, Ann. d. Physik **2**, 780 (1929).

content depends on the so-called frequency spectrum of the body ν_1, $\nu_2, \cdots \nu_n$. It has been proved that the high frequencies asymptotically tend towards the same distribution regardless of the shape of the body. The low frequencies (sound waves) however are essentially dependent on the external shape of the body. This makes the zero point energies $h\nu_{1/2}$, $h\nu_{2/2}, \cdots$ dependent also on the shape of the body and therefore introduces cooperative features into the thermal and caloric behavior of solids.

§3. STATIONARY SYSTEMS, "STATIC" AND "STATIONARY" THERMODYNAMICS

In thermodynamics we investigate the behavior of physical systems, that is the dependence of their pressure, energy, etc., on certain variable *static* parameters such as the density, the temperature, the external electric field, etc. We picture this behavior in phase diagrams, with the parameters as coordinates. The thermal equilibrium of a static system is determined by the condition that a certain function such as the total entropy or the total free energy, etc., is a maximum or minimum. Which one of these functions must be chosen depends on the type of variation which one investigates (adiabatic at constant volume, or isothermal at constant volume, etc.).

Static systems naturally are very special cases of physical systems which in general undergo changes in course of time. If we are looking for a *generalization of thermodynamics* it is logical to consider *stationary systems* as the next step towards the goal of formulating the laws of the macroscopic behavior of systems which change in time.

A stationary system is characterized by the fact that it depends not only on static parameters γ but in addition on at least one dynamical parameter γ' whose value is kept constant with respect to time. Examples of such systems are stationary flows of matter, of electricity, of radiation, or of heat, etc. The behavior of such a system may be geometrically represented in a phase diagram in which at least one dynamical parameter is used. It is immediately evident that in stationary systems the functions which assumed extreme values for static systems no longer possess this property.

Take for instance a long tube which is filled with sodium vapor. If the tube is in equilibrium with a great heat reservoir whose temperature T is constant the total free energy of the gas is a minimum. We may transform this static system into a stationary system by passing lengthwise through the tube ultraviolet radiation of constant intensity. The free energy of the system is then no longer a minimum. This is apparent from the fact that the new system possesses two different temperatures depending on whether we determine it by measuring the average kinetic energy of the gas atoms or the average specific energy of the radiation field. Gases which are distributed throughout the interstellar spaces form actually a system which is analogous to our example. Although the temperature of interstellar space is very low as far as the radiation field is concerned, the atoms nevertheless possess speeds corresponding to 10,000°C or more, because of the ionization and the ensuing recoils caused by the visible and ultraviolet light from the stars which sweeps the spaces.

The following new problem therefore suggests itself. Which functions Γ take the place of the entropy, the free energy, etc., in the case of stationary systems? I shall not here go into detail about this problem. A little consideration, however, shows that the Γ's must be of the form

$$\Gamma = \text{function of } [\gamma, \gamma', B, (\partial/\partial S_i)(\gamma, \gamma')]. \quad (8)$$

Here γ and γ' are the static and the stationary parameters, respectively. Essentially new is the dependence of Γ on the boundary conditions B and on the differential coefficients of the intensive parameters with respect to the spatial coordinates S_i. For our considerations the occurrence of B is important. This means that in stationary systems we necessarily are confronted with *cooperative phenomena*. This conclusion is not only important for the behavior of actually stationary systems but it also has serious consequences with regard to many important characteristics of actually static systems which we find in nature or produce in the laboratory. This peculiar conclusion is related to the existence of thermally *pseudostable systems*. For more details I refer to the next sections.

An interesting stationary system was once

treated by W. Nernst.[4] He investigated the dissociation equilibrium of a gas in a stationary flow of heat. The relative concentrations of the molecules and the particles into which they dissociate not only depend on the temperature T and the pressure p at a given point but also on grad T. This is easily understood because of the diffusion through the boundary of two adjacent volume elements which are held at two different temperatures by the heat flow.

It may not be superfluous to add that there are systems of *apparently stationary* character which nevertheless are governed by the same laws as static systems. This happens when the stationary character of the system is only due to a transformation of coordinates.

For the extension of thermodynamics which I have suggested in the above I propose the name *stationary thermodynamics* in contradistinction to the usual older discipline which might more specifically be called *static thermodynamics*. Whether and how the characteristic canonical functions Γ can generally be determined is a problem for further investigations. Two methods suggest themselves. One is to apply static thermodynamics to differential parts of a stationary system. The second method consists in using statistical methods in investigating certain characteristic statistical games or models.[5] If general methods can be found they will naturally be of great value as stationary systems are very frequent and of great importance. I mention among others: (A) stationary flows of liquids and the problem of turbulence; (B) stationary flows of heat and of electricity; (C) flows of liquids such as blood or saps in plants. An important problem here is how chemical reactions take place on cell walls subjected to stationary flows.

§4. The Problem of the Solid State

Some of the most important applications of our previous considerations lie in the vast field which may shortly be called the physics of solids or more specifically the physics of crystals.

I shall first discuss a few general characteristics of crystals and I shall try to show that cooperative actions between many particles are mainly responsible for the existence of a crystalline state. I then shall describe how such cooperative actions in general necessitate the formation of a *secondary structure of crystals*.

One of the most surprising characteristics of crystals is the existence of an extremely well-defined temperature of the melting point. Indeed, most crystals, if held at constant pressure, melt within a very small range of temperature, the range being usually too small for an actual determination of its width. This fact has been known for a long time, which however does not render it any more comprehensible. As I have explained already in another place[6] the difficulty lies in the following circumstance. If the formation of a crystal lattice were due to the interaction of each of its atoms with a limited number of neighboring atoms then melting, according to statistical mechanics, should be a phenomenon similar to the dissociation of polyatomic molecules containing a corresponding number of atoms. Melting similar to dissociation of polyatomic molecules at constant pressure then would extend over quite a considerable range of temperature. A sharp melting point is comprehensible only if cooperative phenomena between a great number of atoms are responsible for the existence of crystals.

A second fact which points very strongly towards the existence of cooperative phenomena in solids is the surprisingly accurate line-up of crystalline planes over macroscopic distances. Calcite planes for instance are lined up to a few seconds of arc over a distance of one centimeter. It is very difficult to understand this fact on the basis of individual interactions, which, as we know, are greatly disturbed by temperature agitation. It is still harder to understand why even quite appreciable layers of foreign atoms do not disturb the line-up.

In the third place the enormous influence of a few absorbed foreign atoms suggests for its explanation the existence of cooperative phenomena. The recrystallization through grain boundaries which are occupied by many layers of contaminating atoms might be mentioned in this connection also.

[4] W. Nernst, *Boltzmann Festschrift*, p. 904 (1904).

[5] P. and T. Ehrenfest, Encyklopädie d. math. Wissenschaften IV, 2, No. 6, p. 82.

[6] F. Zwicky, Proc. Nat. Acad. Sci. **17**, 524 (1931).

Fourthly, volume effects are known to exist even for crystal grains of macroscopic size.[7]

The phenomena discussed in the above necessitate the existence of cooperative phenomena in crystals. Which particular cooperative phenomenon is responsible for a particular kind of crystal must be decided by a special theoretical or experimental investigation.

As far as the geometrical arrangement of atoms in a crystal is concerned we are now confronted with the following situation. The *primary structure* will essentially be determined by the type of *individual* interaction between neighboring atoms. It may for instance be cubic. On top of this we must consider the action of a certain cooperative phenomenon which may have a symmetry character other than the primary structure, say tetragonal. The cooperative phenomenon will therefore have a tendency to distort the primary structure, this effect being in general a very slight one. If now our crystal had always the shape of a long thin needle its structure would be homogeneous and slightly tetragonal. If, however, the crystal is of any other shape the surfaces will disturb the formation of a uniformly tetragonal structure. At the surfaces the cooperative phenomenon which is characteristic for one crystal will indeed produce results different from those in the interior of the crystal. It would then follow that different effects would be obtained for different shapes of crystals. A crystal also would not possess any equation of state. It can however be shown in special cases that through the formation of a secondary structure a compromise is reached which reconciles the antagonistic tendencies of the individual and the cooperative actions. In the above example this means that the crystal is subdivided into equal regions or blocks whose tetragonal axes alternate in a periodic fashion between the directions $[\pm 1, \pm 1, \pm 1]$. This case is for instance realized if a self-perpetuating electric or magnetic polarization may be set up along any of the three principal directions in a cubical crystal. For details I must refer the reader to a discussion which I have given elsewhere.[8]

Generalizing the above considerations we may state that the antagonistic tendencies of the individual and the cooperative actions between the elementary building stones of a crystal are likely to lead to the formation of a secondary structure, provided that the symmetry characters of the two phenomena are different. If the symmetry characters happen to be the same it is conceivable that ideal crystal lattices may be formed. This might be true for some diamonds. My only support for this statement is that diamond has a slipping strength which seems to be of the order which one expects for an ideal lattice.

Our general conclusion may be stated schematically as follows:

Individual actions ——— primary structure
Cooperative actions——— secondary structure.
The cooperative actions at the same time account for the fact that crystals exist at all.

In regard to the individual interactions between atoms it should be remarked that they cause, statistically speaking, the existence of a primary structure even in the liquid state. This view is supported by the facts which have recently been obtained by the x-ray investigations of liquids.

Finally mention must be made of cooperative phenomena which act during the growth of crystals. In the simplest case of the uniform growth of a crystal in one direction only we are dealing with such a stationary system. The essential characteristic of such a system is that the heat of fusion which is liberated on solidification is carried off in the form of a stationary flow. This flow necessitates the existence of a temperature gradient. This gradient for ordinary rates of growth is great enough to produce a plastic deformation of the crystal in *statu nascendi*, as I have shown in another place.[7] If the crystal is not annealed during the cooling process it will remain in a partially deformed state. The resulting crystal will be thermodynamically pseudostable. This pseudostable configuration therefore is the result of the cooperative phenomenon which is caused by the stationary character of the process of growth. There exist many other phenomena of this type.

§5. REMARKS ON FERROMAGNETISM

Ferromagnetism from all we know must be regarded as a typical cooperative phenomenon

[7] F. Zwicky, Phys. Rev. 40, 63 (1932).
[8] F. Zwicky, Phys. Rev. 38, 1772 (1931).

whose existence is due to the interaction of a great number of elementary particles. Ferromagnetism provides excellent illustrations for some of the contentions of this paper.

Let us discuss some of the characteristics of the simple theory of ferromagnetism due to P. Weiss. He assumes that in a ferromagnetic substance there are N magnetic dipoles μ per cm³ which may freely rotate. If the medium is isotropic and infinitely extended (without any boundaries) the dipoles are acted upon by a total field

$$H_t = H_e + H_m \qquad (9)$$

where H_e denotes the applied field and H_m the so-called molecular field. If the dipoles were of electric origin or if we deal with a gas such as NO whose molecules possess magnetic moments, then

$$H_m = 4\pi I/3, \qquad (10)$$

where I is the intensity of the electric or the magnetic polarization respectively. Weiss showed however that in order to obtain an adequate theory of ferromagnetism one must put

$$H_m = \alpha I, \qquad (11)$$

where α is of the order of 10,000. Quantum mechanics recently has furnished a rational explanation of these high values of α.

Under certain conditions (N large and T small) the above equations result in a permanent magnetization of our substance. If $\bar{\mu}$ is the average magnetic moment per particle in the direction of $H_t = H_m$, assuming $H_e = 0$, then

$$\bar{\mu}/\mu = \text{Coth } x - 1/x$$

$$x = \mu H_m/KT \quad \text{and} \quad I = N\bar{\mu}, \qquad (12)$$

where K is Boltzmann's constant. For $H_e = 0$ and T sufficiently low we have $\bar{\mu} \neq 0$. This resulting permanent magnetization is a typically cooperative phenomenon as the existence of the molecular field $H_m = \alpha N\bar{\mu}$ is caused by a macroscopic amount of matter containing a great number of dipoles. As we have claimed for such phenomena it has a sharp *melting point* at

$$T = \theta = \alpha N\mu^2/3K. \qquad (13)$$

This melting point is usually called the Curie point. Near $T = \theta$ we may expand, as x is small,

and we obtain

$$\bar{\mu}^2 = -45(KT/\alpha N\mu)^3/\mu + 15(KT/N\alpha\mu)^2$$

$$\bar{\mu}^2/\mu^2 = 5(T/\Theta)^2(\Theta - T)/3\Theta, \qquad (14)$$

which is a parabola for $T \sim \Theta$. This results in $\bar{\mu} = 0$ for $T = \Theta$. It is

$$d\bar{\mu}^2/dT = -5\mu^2/3\Theta = -5K/\alpha N$$

or as $\bar{\mu}(\Theta) = 0$ we have $d\bar{\mu}/dT = \infty$ for $T = \Theta$. This means that the melting point of ferromagnetism (its disappearance with T) is infinitely sharp. This is in accordance with our contention that the cooperation of many particles is responsible for the existence of sharp melting points. If a finite system of dipoles were considered the sharpness of the melting point would be decreased because of surface effects and for only a few dipoles cooperating the melting would take on the character of a dissociation spread over a wide range of temperatures.

It goes without saying that ferromagnetism exhibits all the other characteristics of a typically cooperative effect. It indeed implies a lineup of magnetic moments over macroscopic distances. It depends very much on small amounts of impurities present. It is structure-sensitive and it shows volume effects inasmuch as particles of colloidal size do not have the same magnetic characteristics as bigger particles.

Both from the Weiss theory and from the more modern quantum mechanical explanation one would expect in the first approximation a uniform line-up of the magnetic moments in one of the directions of easiest magnetization of a ferromagnetic crystal. This means that such a crystal for $H_e = 0$ should exhibit a permanent magnetic moment different from zero. In reality this is not the case as a single crystal as a whole is unmagnetic. From the caloric behavior, that is, the specific heat, it is known that the permanent magnetization exists. This forces us to assume a subdivision of the crystals into magnetically saturated regions whose moments however balance out over the whole crystal. The reason for this probably lies in the following. If the crystal were magnetized as a whole it would not possess any equation of state because the demagnetizing effect of the surface would depend on the macroscopic shape of the crystal. An energy loss cor-

responds to this as the demagnetizing field is directed oppositely to H_m. This loss can be avoided if the crystal is subdivided into bundles of long needles which are alternately magnetized in opposite directions. Such an arrangement has a demagnetizing field equal to zero. The theory of course is confronted with the task of proving that the loss of energy along the surfaces of the oppositely magnetized needles is less than the loss corresponding to the demagnetizing field of a uniformly magnetized crystal. Experimentally, however, this seems to be established. Assuming this to be correct the elementary regions of uniform magnetization can be found by the procedure suggested previously by Dr. H. M. Evjen and myself. This method suggests the following subdivisions or *magnetic secondary structures* for Co, Ni and Fe.

Cobalt is hexagonal with the direction of easiest magnetization along the hexagonal axis. The simplest magnetic secondary structure would be obtained if needles parallel to the hexagonal axis and of triangular cross section are alternately magnetized in opposite directions. In the basal plane we would have an arrangement as shown in Fig. 1. Shading means magnetization
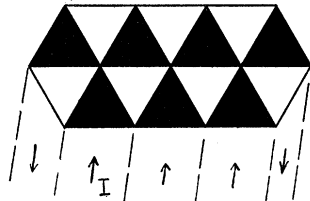

FIG. 1. Basal plane of cobalt.[9]

upwards. The other needles are magnetized downwards. If needles of hexagonal cross section are used a symmetrical arrangement can only be obtained if three states of magnetization are admitted, upward (+), downward (−), and zero (0) which would give the picture (2). The two arrangements would be different in regard to the caloric behavior of the crystals. If therefore from the caloric behavior complete saturation of the

crystal can be deduced an arrangement of the type of Fig. 1 must be chosen.

It is well known that a type of magnetic secondary structure in Co has been found by F. Bitter[10] who observed that F_2O_3 colloidal particles will settle in regular arrays on Co crystals. The particles settled in an array similar to a dense star field on the basal plane and in straight lines in a plane parallel to the hexagonal axis. This is in accordance with our suggestion of needles parallel to the hexagonal axis being alternately magnetized in opposite directions. The thickness of the needles is experimentally of the order 10μ.

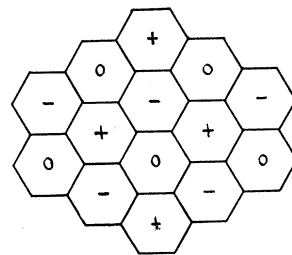In nickel which is a cubic crystal the direction of easiest magnetization is along the body di-

FIG. 2.

agonal [111] of the cube. An adequate secondary structure is obtained by magnetizing alternately needles with a square cross section. The needles must be parallel to one of the three principal directions of the cube and the largest uniformly magnetized regions will be cubes with the resultant magnetic moment in the direction of one of its body diagonals.

F. Bitter has not obtained any patterns of the settled colloidal particles in this case for a zero external field. This means that the secondary structure is characterized by a lattice constant which is too small to be resolved by his method. If a field is applied, however, the particles settle in equidistant straight lines which are approximately normal to the applied field. This might be interpreted in the following way which is in accordance with our previous considerations. One would expect off-hand that on application of an external field H_e the whole magnetic secondary

---

[9] Notice that the two types of triangles are mirror images. In which way this fact provides a very simple illustration for the existence of a secondary structure in many crystals will be discussed in one of my next publications.

[10] F. Bitter, Phys. Rev. **38**, 1903 (1931) and **41**, 507 (1932).

structure would disappear and that the crystal would appear uniformly magnetized along that diagonal of the elementary crystallographic cube which is nearest to the direction of H_e. This, however, would result in a maximum demagnetizing effect of the surface. It seems therefore energetically more advantageous to make use of more than one, and, may be, of all four space diagonals choosing on every one, of course, that direction which is nearer to the direction of the external field. This would result in an alignment of the magnetic vectors which in a two-dimensional representation is schematically shown in Fig. 3. Although the magnetic stray fields are
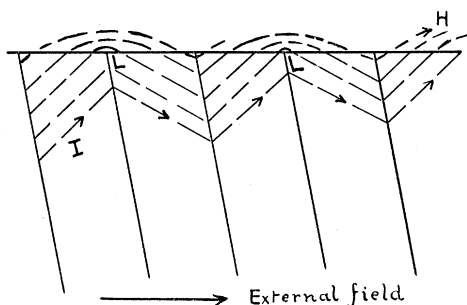

FIG. 3. Nickel in a magnetic field.

present all over the surface the colloidal particles would be drawn in only at places where the field is strongly inhomogeneous and would settle along the lines L, which agrees qualitatively with F. Bitter's findings. An experimental investigation is under way in this Institute to measure out the distribution of the magnetic stray fields on the surface directly. From this investigation much more detailed information about the phenomenon in question may be hoped for.

In iron the direction of easiest magnetization is along the principal axes of the elementary cube, that is, along one of the axes $[\pm 1, 0, 0]$, $[0, \pm 1, 0]$ or $[0, 0, \pm 1]$. The elementary cells of the magnetic secondary structure therefore must be alternately magnetized along one of these six directions. Two relatively simple solutions suggest themselves. The elementary cells of the first solution are regular octahedra and tetrahedra, whose four essentially different faces are respectively normal to the space diagonals of the elementary cube of the primary structure. The second solution uses regular rhombic dodecahedra with faces which are respectively parallel to the twelve planes of the type (110). This latter solution cannot be built up by an interpenetration of sets of infinite needles. In both solutions the elementary cells of the secondary structure are alternately magnetized in the principal directions $[1, 0, 0]$, etc. As iron single crystals do not seem to possess any crystallographically distinguished slip planes the solution using rhombic dodecahedra seems to be the more adequate. However, further experimental investigations will be necessary to solve the problems related to the geometry of the magnetic secondary structure of ferromagnetic crystals.

Just as in the case of nickel the characteristic spacing of the magnetic secondary structure in iron is too small to be resolved by Bitter's method. With an applied external field however one obtains striations similar to the case of nickel.

Bitter's experiments prove without any doubt the existence and intrinsic importance of cooperative phenomena. As the striations which he obtains may be shifted at will relative to the boundaries of the crystal it is impossible to make imperfections (or mosaic structure) responsible for the phenomena in question. The effects discovered by him therefore prove conclusively the possibility and the actual existence of secondary structures as I have postulated them several years ago.

This short sketch may suffice for the present to make clear the vital importance of cooperative phenomena for a deeper understanding of the nature of the crystalline state. As mentioned before, cooperative actions between many particles are not confined to crystals. They play an important part in other systems and are probably most essential for the possibility of living organisms.