

PERMANENT ELECTRIC AND MAGNETIC MOMENTS OF CRYSTALS

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(Received September 19, 1931)

ABSTRACT

In the first part of this paper the conditions for the existence of self-perpetuating electric moments in crystals are discussed. If these conditions are satisfied, the crystals must either show macroscopic electric moments or they will necessarily possess a definite type of a secondary structure. Certain complications may come in, however, if one is dealing with metals. Finally, the analogous magnetic case is qualitatively discussed.

§1. INTRODUCTION

THE theory of the ideal crystal lattices must be regarded as a complete failure as far as the treatment of structure sensitive properties is concerned. I have recently endeavored to show that a satisfactory theory of the physics of solids can be developed by introducing a secondary structure of crystal lattices.¹ This structure in general may be described as a periodic, very slight variation in density. I arrived at the conception of a secondary structure from purely theoretical arguments which threw doubt on the current conception of ideal crystals being thermally stable. Although many important conclusions of this theory were verified experimentally, its foundations are not very satisfactory for the following reasons.

In the first place, the procedure which I followed did not supply any unambiguous way of determining the exact nature of the deviations which transform an ideal lattice into a real and thermally stable crystal.

In the second place, it was very difficult to account for dimensions of the secondary lattice larger than a few hundred Angstroms, such as we have been finding in single crystals of metals. Although the theory does not really enable one to derive accurate values for the lattice constant D of the secondary structure there are strong reasons for assuming that approximately

$$D = d/(1 - d_p/d) \tag{1}$$

Here d is the ordinary lattice constant and d_p the corresponding spacing of a single plane of atoms which in itself is assumed to be in equilibrium under its own forces. The relative change from d to d_p can be estimated to be of the order of one percent, which according to (1) makes values of D larger than $100d$ very improbable. It also has been objected that it would be very hard to understand how actions over such large distances come about.

In the third place, experimental investigations carried out on single crystals suggest that there are secondary lattices of very different types. The theory therefore is confronted with the task of finding as many effects as

¹ F. Zwicky, Proc. Nat. Acad. Sci. **15**, 816 (1929); Helvetica Physica Acta **3**, 269 (1930); and **4**, 49 (1931).

possible which will render an ideal crystal thermally unstable. In addition, one has to try to find, if possible, a common denominator for all these effects. In a recent publication² I have advanced a tentative solution of this latter problem. The essence of my proposal was that those effects which are mainly responsible for the formation of a crystal at the same time necessitate a secondary structure. Those effects were recognized to be simultaneous cooperative actions between many particles. It seems therefore desirable to investigate more closely the characteristics of such actions. In this paper one very special phenomenon which depends on the cooperation of many particles will be considered. Its character will be best understood by studying some of its essential features in relation to a simple lattice.

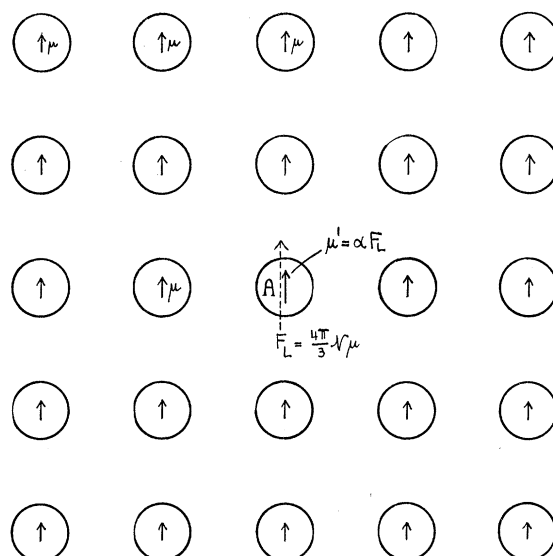


Fig. 1. Lattice of self-perpetuating dipoles.

§2. GENERAL REMARKS ON SELF-PERPETUATING ELECTRIC MOMENTS

The essential part of this paper is devoted to a generalization of K. F. Herzfeld's considerations concerning the characteristics of metals. Herzfeld derives a criterion which decides whether or not an element will occur as a metal. His argument is roughly as follows:³

Consider a simple cubic lattice occupied by atoms whose dielectric constant is α . (See Fig. 1.) Suppose that all the atoms except A are endowed with an infinitely small electric dipole μ . Then because of the action of the μ 's there will be an electric field at A which is equal to $F_L = 4\pi P/3 = 4\pi N\mu/3$, where N is the number of atoms per unit volume and P the polarization per unit volume.⁴ The average field throughout the crystal of course is zero,

² F. Zwicky, Proc. Nat. Acad. Sci. September, 1931.

³ H. F. Herzfeld, Phys. Rev. **29**, 701 (1926).

⁴ See for instance P. Debye in Handbuch d. Radiologie, Vol. VI, p. 600.

provided that the lattice is infinitely extended. The so-called Lorentz field deforms the atom A and endows it with a moment μ'

$$\mu' = 4\pi N\mu\alpha/3. \quad (2)$$

Suppose now that

$$4\pi N\alpha/3 = 4\pi N\alpha\rho/3M = R\rho/M > 1 \quad (3)$$

where R is the molar refractivity, ρ the density, M the molecular weight, and $N = 6.06 \times 10^{23}$. It then follows that

$$\mu' > \mu.$$

This means that the assembly of the induced dipoles is a self-perpetuating configuration of ever increasing moment. The process stops, of course, as soon as all the atoms are stripped of their loosest electrons. Condition (3) therefore is a condition for the element to be a metal.

It is very important to notice that the conclusions drawn above are valid only if α either increases or at least stays constant with increasing μ . This is probably generally true if α is the polarizability of an atom. We may, however, generalize Herzfeld's theory to systems with elementary units other than atoms, as will be shown in the next section. It then happens that the respective dielectric constant decreases with increasing polarization. The system involved may then jump into a configuration of permanent electric polarization without this process resulting in a collapse of the elementary particles, such as the stripping of atoms of their electrons. The permanent electric polarization need not be apparent in macroscopic dimensions, as will be shown later. In the case of a resulting macroscopic moment we are dealing with a crystal which possesses the characteristics of an electret. If only microscopic regions are electrically polar, they may compensate each other over large distances. We then obtain a peculiar type of a secondary structure.

In the next section we shall discuss the properties of a definite simple lattice which, however, is chosen so as to exhibit all the general features in which we are interested in our discussion.

§3. PERMANENT ELECTRIC POLARIZATION IN CUBIC FACE CENTERED IONIC LATTICES

We investigate the properties of a lattice which is built up of positive and negative ions. We assume that for the mutual potential energy of two ions i and k we may write, as usually adopted for a first approximation,

$$\epsilon_{ik} = e_i e_k / r_{ik} + A / r_{ik}^p \quad (4)$$

where A and p for simplicity are taken to be the same for all the three possible combinations of the two ions.

The average energy ϵ of an ion in the face centered cubic lattice can be shown to be

$$\epsilon = -1.747e^2/r + \gamma A/r^p \quad (5)$$

with r designating the usual lattice constant. Numerical values of γ for different p 's are tabulated in Table I.

TABLE I.

p	5	6	7	8	9	10
γ	166	269	478	888	1700	3287

Now for this lattice to be in equilibrium we must require

$$\frac{\delta\epsilon}{\delta r} = 0 \text{ for } r = d \quad (6)$$

or

$$A = 1.747e^2d^{p-1}/p\gamma. \quad (6')$$

It is usually assumed that this condition is all that is required in order to make a lattice of the described type dynamically stable. Indeed, in all the cases dealt with in the literature it was found that a lattice of the above type, with A equal to (6') is also stable against a linear extension, shearing, or against a displacement of the whole negative lattice relative to the positive lattice, etc. However, there was known no general proof that condition (6) insures the complete dynamic stability of the lattice. In fact, it can be shown that this is not at all the case. For this purpose we shall investigate more closely the stability of our model with regard to relative displacements of the negative and the positive lattice. Such displacements evidently may be caused by external electric fields. It is well known that the characteristic frequencies involved correspond to the frequencies of the residual rays.

Suppose that the lattice of the positive ions is given a uniform infinitesimal displacement ξ in the direction of the [100] axis. At the location of each ion a Lorentz field

$$F_L = 4\pi P/3 \quad (7)$$

is created, with (7') $P = Ne\xi/2$ and $N = 8/d^3$

$$F_L = 16\pi e\xi/3d^3. \quad (8)$$

The energy per molecule (negative and positive ion) is equal to

$$\Delta u^- = -e\xi F_L/2 = -8\pi e^2\xi^2/3d^3. \quad (9)$$

There is also a change of energy Δu^+ due to the forces of repulsion. Summing up the individual contributions of all the neighboring atoms one finds for Δu^+ per molecule

$$\Delta u^+ = 4p(p-1) \left[2^p + \frac{4}{9} \left(\frac{2}{3^{1/2}} \right)^p + \frac{4}{5} \left(\frac{2}{5^{1/2}} \right)^p + \frac{4}{9} \left(\frac{2}{3} \right)^p + \dots \right] \frac{A}{d^{p+2}} \xi^2. \quad (10)$$

Values of the numerical factor (h) for different p 's are tabulated in Table II.

TABLE II.

p	5	5	7	8	9	10
h	2680	7860	21800	57700	148000	369000

For the total change of energy per molecule we obtain, therefore,

$$\begin{aligned}\Delta u &= [-8.4e^2/d^3 + hA/d^{p+2}]\xi^2 \\ &= 1.75e^2/d^3 \times [-4.8 + h/p\gamma]\xi^2.\end{aligned}\quad (11)$$

The numerical values of $h/p\gamma$ are given in Table III.

p	5	6	7	8	9	10
$h/p\gamma$	3.23	4.87	6.51	8.10	9.67	11.2

From this table we derive the remarkable conclusion that Δu for p slightly smaller than 6 becomes negative. This is a very remarkable result indeed. It means that a cubic crystal of the described kind will voluntarily jump into a state of permanent electric polarization. Unlike the analogous case of atoms, no destruction of the lattice will take place because of the fact that it becomes

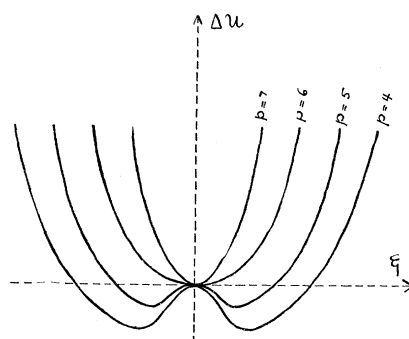


Fig. 2.

more and more difficult to move the two lattices apart as ξ increases. The self-perpetuating movement of the two lattices will therefore stop at some definite value ξ_0 of ξ . Fig. 2 shows the energies Δu plotted schematically as a function of ξ for different values of p . The ideal crystal is dynamically stable with regard to a variation ξ only if $p > 6$. For $p < 6$ it is dynamically unstable. The equilibrium position in this case is given by the minimum of Δu . It corresponds to a state of permanent electric polarization.

The most important result of the above investigation is this. Suppose that we build up a model of a crystal lattice by assuming a certain potential energy function for the mutual interaction of the two particles in the lattice. This energy function may contain certain parameters, A and p in our case. If A and p are determined by adjusting certain characteristics of our model to certain given experimental data (lattice constant, compressibility), one cannot be assured that the model is dynamically stable. Indeed, the particular model discussed above is stable against a uniform pressure because of A having been properly adjusted by (6'). The model also turns out to be stable if a linear extension or a shear is considered. However, for $p < 6$ it is unstable against a relative motion of the positive and negative partial lattices.

§4. GENERALIZATION OF THE MODEL USED IN THE PREVIOUS SECTION

It is obvious that the computations given in the previous section need to be generalized in various ways.

In the first place, our calculation involves implicitly the assumption that no change of dimensions normal to the relative displacement ξ of the two partial lattices is involved. This is certainly not correct, and additional terms must be introduced. For the present discussion it is sufficient to notice that this lateral effect can only increase the initial instability of the lattice.

In the second place, it will be necessary to compute Δu to higher order terms in ξ in order to determine the final equilibrium position ξ_e . It will, however, be of interest to do so only if one is sure that a certain model actually is a good approximation of the real crystal. More about this will be said in section 5.

In the third place, we must take into account that the ions themselves are deformable. The Lorentz field is as before $F_L = 4\pi P/3$. The expression (7') for the total moment P per cm^3 is changed to

$$P = N\mu/2 + N\mu_0 \quad (12)$$

with

$$\mu = e\xi \quad \mu_0 = \alpha F_L \quad (13)$$

if we use the same notation as in the previous section. Therefore

$$F_L = 4\pi N/3 [e\xi/2 + \alpha F_L] \quad (14)$$

or

$$F_L = 2\pi N e\xi / (3 - 4\pi N\alpha). \quad (15)$$

It is evident from the order of magnitudes of $N \sim 10^{23} \text{cm}^{-3}$ and $\alpha \sim 10^{-24} \text{cm}^3$ that the denominator may be considerably smaller than 3, or F_L considerably larger than the corresponding expression with α equal to zero.

In order to get an idea about the magnitude of the Lorentz fields and the corresponding energies involved, we assume that our model has a lattice constant equal to that of rock salt, $d = 5.6 \times 10^{-8} \text{cm}$. For $\xi_e = 10^{-10} \text{cm}$ we obtain $F_L = 1.36 \times 10^6 \text{volts}$. The energy per molecule due to this field is

$$\Delta u^- = \Delta u_1^- + \Delta u_2^- = -e\xi/2 - \alpha F_L^2/2 \quad (16)$$

or in our case $\Delta u_1^- = -1.06 \times 10^{-16} \text{ergs}$. The energy Δu^- is proportional to ξ^2 . It therefore can easily assume values equal to kT say near to the melting point, with ξ amounting to only a few percent of the lattice constant. This is very important because of the fact that certain phenomena may be observed calorimetrically without being easily detectable by a structure investigation with x-rays.

§5. ON A NEW TYPE OF A SECONDARY STRUCTURE

We are now coming back to some of the ideas which have already been mentioned in the introduction.

Suppose that we are dealing with an ionic cubic face centered lattice whose equilibrium configuration is characterized by a permanent electric polarization, due to a value $p < 6$ in relation (4). It is obvious that there are

forces operative during the growth of the crystal which tend to prevent its building up an electric moment. These forces originate on the necessarily existing surfaces. If, for instance, the crystal grows as a large plate a depolarizing field equal to $4\pi P$ will be set up by the surfaces if P is directed normal to the plate. This because of the bound surface charges originated by the electric polarization itself. If the external shape is a sphere or a cube the depolarizing field will be $4\pi P/3$, which still is sufficient to compensate for the Lorentz field. The neutralizing action of the surfaces can be disregarded only if the crystal grows in form of a long needle or if there are charges present which compensate for the action of the surfaces by covering them with charged layers. The bound and the real charges on a surface in this case form double layers with no corresponding external fields. It seems very artificial and unsatisfactory to introduce accidental conditions of this kind. If possible the crystal will favor some kind of an arrangement which allows it to assume

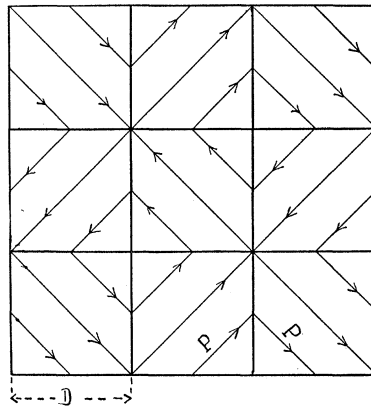


Fig. 3. Permanent electric polarization in crystals.

the configuration of lowest energy without making use of any special external condition. Arrangements of this kind probably must possess the same symmetry character as the primary structure. Fig. 3 gives an illustration of a possible arrangement. It is based on the idea of avoiding neutralizing surfaces by arranging the Lorentz field vectors in circles or in squares conforming with the cubic character of the primary structure as nearly as possible.

In a three-dimensional lattice the secondary structure resulting from a self-perpetuating polarization may be derived by the following simple method, which has been suggested to me by Dr. H. M. Evjen. First think of the crystal being subdivided into identical square needles which are parallel to the $[100]$ direction. Polarize these needles alternately in the $[100]$ and $[\bar{1}00]$ directions. This process is now repeated for the $[010]$ and the $[0\bar{1}0]$ direction in such a way that each intersection of three needles is a cube. The resulting vectors representing the polarization evidently will lie in one of the four space diagonals of the cube.

From Fig. 3 it is evident that the crystal will exhibit a certain peculiar type of secondary structure. In the thermodynamically stable state this

structure may be expected to be an absolutely regular one characterized by a greater lattice constant D . An approximate relation between D and the usual smaller lattice constant d may be derived as follows:

The permanent electric polarization causes a relative change Δ in dimension lateral to it. We consider two adjacent regions whose vectors P are at right angles to each other. These two regions can be approximately in phase with each other only over a distance smaller than $D = d/\Delta$. In fact, if a positive and negative ion face each other at A , then at a distance $D/2$ away from A , two ions of the same sign are in opposition, provided that the dividing line between the two parts of the crystal is of the type $[100]$. We therefore have to keep our regions in Fig. 3 smaller than D or we will begin to lose energy along their boundaries. This means that the new type of a secondary structure proposed in this section is characterized by a greater lattice constant approximately equal to

$$D = d/\Delta. \quad (17)$$

We have seen in section 4 that values of ξ_e equal to 10^{-9} cm lead to reasonable moments such as have been observed in certain crystals, Rochelle salt, for instance. The quantity Δ will of course depend on ξ_e and therefore have a very wide spread. In general Δ will be very small. Therefore

$$D \gg d.$$

This is a very satisfactory result, inasmuch as it may provide an understanding of such remarkably large spacings of the order of 1μ as we have observed for the secondary structure of certain metals. It is a very interesting problem to find out whether the observed secondary structure of metal single crystals can be traced back to the origin proposed here. Although I cannot offer a complete solution of this problem, I should like to advance some tentative suggestions which might prove valuable.

According to the theory of Herzfeld which I have sketched in section 2, electrons are stripped from sufficiently dielectric atoms embedded in solid matter. If the polarizability is increasing with increasing moment, we must conclude that the electrons try to get away from the remaining ions as far as possible. This behaviour, which seems very strange at first sight, is due to the existence of a self-perpetuating polarization. We therefore arrive at the following picture of a metal with say one stripped or free electron per atom. We suppose these atoms to be arranged in a face-centered cubic lattice. The electrons will exhibit a tendency to arrange themselves in a similar lattice which, however, is displaced by half the lattice constant in one of the principal directions say $[100]$. Electrons and ions are thus in the same relative position to each other as the ions in NaCl. This is the picture of a simple metal which F. Haber has advanced many years ago. Of course one must not think of such an arrangement as a static one. If it were static the lattice formed by the electrons could be detected with x-rays, which is not the case. The problem to be solved is to find the interaction between the electron lattice or electron gas and the remaining ions. From the fact that a static arrangement

of charges is unstable (law of Earnshaw), it seems probable that the interaction between the two lattices is such that a simplified expression for the mutual energy of an electron and an ion would require an exponent $p < 6$. This suggests that metals form crystals whose equilibrium configurations are characterized by permanent electric moments. The formation of macroscopic moments would again be prevented by the building up of a secondary structure. From this viewpoint the large lattice constants $D = 5000\text{--}20000\text{\AA}$ which we have observed in different metals appear comprehensible.

Finally, a few words about the alkali-halides. For most of them $p > 6$. Therefore they do not fall within the range of our present considerations, unless a combination of a relatively small p together with a large polarizability α makes them eligible for a secondary structure of the type described above. This may be the case, for instance, for PbS. According to (15) F_L must be multiplied by a factor

$$f = 3/(3 - 2\pi/\Gamma)$$

if α is not neglected. Here $\Gamma = a^3/2\alpha$ and $a = d/2$. Now for PbS we have $\Gamma = 2.54$ and therefore $f \sim 6$. This would put PbS into the category of crystals with permanent moments in microscopic regions, for almost any value of p , which may be the explanation of why PbS and PbTe behave so differently from the other alkali-halides.

§6. PERMANENT MAGNETIC MOMENTS OF CRYSTALS

A ferromagnetic crystal may in some respects be regarded as the magnetic analogue to a crystal possessing a permanent electric moment. However, there are some conspicuous differences between the two cases. In the electric case the back coupling of the induced dipoles is established by the Lorentz field $F_L = 4\pi P/3$. To account for the ferromagnetism in Fe, Ni, Co, etc. according to P. Weiss back-coupling fields of the order 10000 M must be introduced, where M is the magnetic polarization per unit volume. In spite of this enormous back-coupling factor, namely 10000 instead of $4\pi/3$, a single crystal of iron is not magnetic as a whole. This is a very puzzling fact. Indeed it is hard to understand why the crystal should not be uniformly magnetized, as the largest possible demagnetizing factor 4π falls far too short from compensating the enormous factor 10000. This problem has not found a satisfactory solution so far. Whatever this solution may be, it seems safe to conclude that it must involve the existence of a secondary structure of magnetic origin. For, although an iron crystal is not magnetized as a whole it must be magnetized in parts, because of the magnetization betraying itself in the caloric behavior of the crystal (rise of the specific heat below the Curie point, etc.). A magnetic secondary structure therefore exists. Off hand it is impossible to say whether the elementary regions are fibers or cubic blocks or of some other shape. However considerations analogous to those leading to Fig. 3 make it possible to determine the exact shape. Assuming them to be cubic, F. Bitter⁵ has suggested various ways for estimating their size. He finds that they contain

⁵ F. Bitter, Phys. Rev. **37**, 91 (1931).

approximately 350000 atoms each. If we wish to make a theoretical estimate we must apply some relation similar to the one used in the electric case (17)

$$D = d/\Delta$$

where Δ now stands for the relative change in length due to magnetostriction caused by the magnetic saturation. Unfortunately there is no way so far to obtain Δ . If Bitter's estimates are correct, then Δ must be of the order of 1 percent.

It is very interesting to notice that ferromagnetic crystals behave abnormally in regard to plastic deformation. Single crystals ordinarily glide along certain planes belonging to a discrete crystallographically determined set. In iron, however, only the [111] direction is distinguished, but any plane through it may be a slip plane.⁶ This becomes comprehensible if one considers that the elementary parts of the magnetic secondary structure of iron are slightly tetragonal. Adjacent blocks are in phase only for distances less than 200A making use of Bitter's estimate. Iron is therefore, in a way, much more similar to an amorphous substance than to other metal crystals whose secondary structures are characterized by spacings of the order of 1μ . It is to be hoped that if iron single crystals are annealed and distorted in a magnetic field that they also will exhibit definite crystallographic slip planes. Experiments to check this are being carried out at this Institute.

§7. CONCLUDING REMARKS

I have recently proposed a scheme which was intended to provide a general working basis for the physics of crystals. I showed that those phenomena which essentially characterize the crystalline state are due to the simultaneous cooperation of many particles in regard to a line-up in space. There are different types of such cooperative effects. The main purpose of this paper is to point out two of them which are related to the formation of permanent electric and magnetic moments in crystals. I also attempted to show in which way these two effects may be the cause of a secondary structure of crystals.

⁶ G. I. Taylor and C. F. Elam, Proc. Roy. Soc. **A112**, 337 (1926).