

REMARKS ON SUPERCONDUCTIVITY

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1. *Introduction.*—Great efforts have been expended on the electron theory of metals during the last thirty years. The classical theory was at fault because it considered the electrons as entirely free. The quantum theory partly remedied this fault. In the first place, through application of the exclusion principle, the interaction between the electrons was *schematically* taken into account. In the second place the effect of the remaining ion lattice was introduced by placing the electrons into a fixed triply periodic field of force, corresponding to the distribution of the positive metal ions over the lattice. The results of all these efforts are still far from satisfactory. In particular the phenomenon known as superconductivity has so far defied all explanation.

The ultimate failure of the various versions of the electron theory of metals is not entirely surprising. Indeed none of these theories embraces those effects which make a metal a metal. It seems clear that any theory of metals can be satisfactory only if it contains some fundamental premises which essentially account for the distinction between metals and non-metals. Such a criterion was given by K. F. Herzfeld.¹ This criterion is related to the mutual interaction of all the free electrons with the remaining ion-lattice.

2. *On Coöperative Phenomena in Metals.*—According to Herzfeld the so-called Lorentz field causes a self-perpetuating polarization in any substance whose molar refraction satisfies a certain condition. In the case of a cubic crystal or any isotropic substance (liquid) this condition is

$$4\pi N\alpha/3 > 1. \quad (1)$$

Here N is the number of atoms per cm.^3 , and α is the polarizability of the atoms. We have assumed that there is only one kind of atoms involved. The self-perpetuating polarization causes the atoms to be stripped of one or more of their electrons. As a result the electrons tend to occupy regions which are near the centers of the interspaces between the remaining ions. At sufficiently low temperatures ions and electrons will arrange themselves in a lattice. The electron lattice must of course be thought of as a dynamical average, as a static lattice would be unstable. The contention of this paper is that *this* type of an electron lattice must be subjected to a quantum mechanical investigation if one wishes to obtain a satisfactory theory of metals. Furthermore it must be noticed that the interaction of the ion-lattice with the electron-lattice again results in a self-perpetuating polariza-

tion (slight additional displacement of the two lattices relative to each other). I have previously discussed this type of polarization² in the case of heteropolar lattices such as LiF, NaCl, etc. I have also described how this polarization may cause the formation of secondary structures.

The consideration of coöperative phenomena of the type described, in conjunction with the introduction of a secondary structure, furnishes rational explanations for three groups of phenomena which are incomprehensible on the theory of ideal crystallographic lattices.³ These phenomena are:

(a) The existence of *structure sensitive* properties in crystals. In particular it is now possible to give a rational explanation of the peculiar mechanical properties of crystals, including the extraordinary effects of cold working⁴ and the actions of impurities.

(b) The occurrence, in crystals, of *characteristic lengths* of the order of $D = 10^{-4}$ cm. in contradistinction to the ordinary lattice constants of the order of 10^{-8} cm. Such lengths of the order of 1μ play an important rôle in recent theories of the frequency dependence of ferromagnetism, of recrystallization and of the plasticity of crystals. They also seem to be indispensable for the understanding of surface phenomena of crystals.

(c) The existence, in crystals, of one or more extremely sharp *transition points*, such as the melting point, the transformation points between various crystallographic modifications, the pseudo-transformation points, the Curie points and the abrupt changes of the direction of magnetization.

In the following I shall try to show that superconductivity is a phenomenon which also possesses the characteristics (a), (b) and (c). Superconductivity, therefore, must be related to those coöperative phenomena and secondary structures which are characteristic for the metallic state.

3. *On Superconductivity.*—The following are some of the characteristics of superconductivity.

(a) Superconductivity is greatly affected by plastic deformation, by the introduction of small amounts of impurities and by the magnetic field. It is therefore a structure sensitive property.

(b) Superconductivity can be made to disappear if the frequency of the induced current is increased beyond a certain limit. This fact can be explained if one assumes the existence of a surface layer of approximate thickness 10^{-4} cm. which can never be superconductive.⁵ This layer exhibits the ordinary high resistance, and the dependence on frequency of the total resistance in the superconductive state can be interpreted on the usual theory of the skin effect. If this interpretation is correct superconductivity depends on a characteristic length of the order of 10^{-4} cm.

(c) Superconductivity is subject to *sharp transitions* inasmuch as it disappears abruptly at a definite temperature T_s . It also can be destroyed by the application of a magnetic field of rather definite magnitude. The rela-

tions between resistance and temperature resp. magnetic field very often exhibit hysteresis effects. This again indicates that superconductivity is a structure sensitive phenomenon.

From this enumeration it becomes evident that the problem of the superconductivity in many important respects is analogous to the problem of the existence of a crystalline state of matter. Indeed both problems involve analogous sets of characteristics (a), (b) and (c). I have previously proposed that the problem of the crystalline state may find a solution in the consideration of certain coöperative phenomena and related secondary structures.³ Assuming that this contention is correct we may expect to find on the same grounds a solution for the problem of the superconductivity.

Our picture therefore is approximately as follows: The self-perpetuating polarization, or some similar phenomenon, which describes the coöperative interaction of the electron-lattice and the ion-lattice in a metal is responsible for the crystallization of this metal. It can be shown that this interaction at a definite temperature T_p is abruptly destroyed (similar to ferromagnetism). On our views this temperature T_p must be identified with the temperature T_m at the melting point. Consequently the energy of polarization ϵ_p (which is of the order of 10^{-14} ergs to 10^{-13} ergs per atom) must approximately be equal to the heat of fusion per atom. However, not all of the electrons in the metal are to be regarded as permanent members of the electron lattice. The thermal electrons (tail of the Fermi distribution) form an electron gas which is in thermal equilibrium with the electron lattice. For this electron gas there now exists another *second* chance to crystallize. Indeed, because of the formation of a secondary structure, the energy is not the same for all of the atoms in the crystal. In the "secondary" planes this energy will have some slightly different value, ϵ'_p such that

$$|\epsilon_p - \epsilon'_p| \ll |\epsilon_p|. \quad (2)$$

The crystallization of a part of the thermal electrons in an arrangement which is predetermined by the secondary structure will take place at a temperature which is approximately given by

$$T_s = T_m |1 - \epsilon'_p/\epsilon_p| \ll T_m. \quad (3)$$

If we identify T_s with the transition temperature of superconductivity we obtain at once an explanation of why this temperature is of the order of only 1° Kelvin. Why our secondary electron lattice may move through the crystal with practically zero resistance must be made the subject of a quantitative investigation. I mention here only that the ripples of the field of force (or the potential) along the secondary planes are very much flattened out as compared to the field of force throughout the more ideal

parts of the crystal. I have previously made use of this fact to explain the low mechanical strength of crystals against gliding (the word low is to be understood in comparison with high torsional moduli). Low mechanical gliding strength and superconductivity in our picture are closely related phenomena. It might be possible to obtain a check on this far reaching conclusion by closely investigating the gliding strength just below and above the transition point of a superconductor.

The above considerations do not claim to give more than a suggestion for a new theoretical basis on which the so far completely obscure superconductivity might be understood. A few more details may be mentioned which seem to furnish more support for our considerations. In the first place the characteristics (*a*), (*b*) and (*c*) find a rational explanation.

In the second place the difficulties related to the effects of grain boundaries in polycrystalline aggregates become less grave. These grain boundaries represent potential thresholds which would make superconduction impossible if this conduction were caused by the optical emptiness of ideal crystal lattices at low temperatures. The secondary structure, however, being the result of certain coöperative phenomena, can be expected to establish relations between neighboring microcrystals, even in the case that considerable amounts of impurities are present in the grain boundaries. The fact that such relations exist is suggested independently by some peculiar characteristics of the process of recrystallization and the resulting shapes of the grain boundaries.

In the third place the following important experiment can be understood. In a superconducting lead sphere a current around a certain diameter is induced. If the lead sphere is rotated around another diameter the current is partly carried along, that is, its axis of symmetry is turned. This fact would be incomprehensible if superconductivity were a volume phenomenon.

In the fourth place it is very important that the action of a magnetic field in reëstablishing a high resistance in a superconductor seems to be due to an action of the field on some predetermined arrangement of the elementary particles in the crystal. For a detailed account of this conclusion the original paper of de Haas should be consulted.⁶

4. *On Characteristic Lengths in Crystals.*—In the above a characteristic length D of the order of 10^{-4} cm. has been mentioned. With regard to its possible character I shall very briefly discuss a few characteristic lengths which can be constructed by combining some of the fundamental physical constants. A length of nuclear dimension is

$$\delta = e^2/mc^2 = 2.8 \times 10^{-13} \text{ cm.} \quad (4)$$

For mutual interactions with other particles, at relative distances δ , the electrons probably entirely lose their individualities;⁷ δ therefore also may

be regarded as a lower limit for the applicability of the exclusion principle.

A length of atomic dimensions is

$$d = h^2/me^2 = 20.8 \times 10^{-8} \text{ cm.} \quad (5)$$

(The first hydrogen Bohr orbit has a radius $h^2/4\pi^2me^2$.) This length d may also be taken as the prototype of a crystal lattice constant.

Making use of the dimensionless fine structure constant $\alpha = 2\pi e^2/hc$ two more significant lengths may be constructed,

$$D_1 = d/\alpha = 137d$$

and

$$D_2 = d(M/m)^{1/2}/\alpha \quad (M = \text{mass of an atom}). \quad (6)$$

It can be shown that these lengths characterize the greatest region in which coöperative phenomena of the type of a self-perpetuating polarization can possibly establish uniform conditions. This limitation with regard to the radius of action is due to the finiteness of the speed of all physical signals.

The length D_1 also limits the size of a region in a crystal to whose electrons the exclusion principle in its usual form may sensibly be applied.

As the self-perpetuating polarization is intimately related to the highest frequencies of a crystal lattice, the lengths D_1 and D_2 may play a rôle in the determination of the lattice constants of secondary structures.

Still other characteristic linear dimensions can be constructed if one introduces great dimensionless numbers which necessarily occur wherever coöperative phenomena play a rôle. I have shown in another place² that d/Δ may be significant, where Δ is the relative electrostriction or magnetostriction resulting from a permanent electric resp. magnetic polarization of a crystal.

So far the exact theoretical determination of the secondary lattice constants of crystals has not been possible. The difficulty of finding a solution of this problem becomes evident if one considers the following inequalities,

$$|\epsilon_t| \gg |\epsilon_p| \gg |\epsilon_p - \epsilon'_p| \quad (7)$$

where ϵ_t is the total energy of binding of a given particle in the crystalline state. The determination of the secondary lattice constant depends on the variations of the quantity $(\epsilon_p - \epsilon'_p)$ as one varies the dimensions of the secondary structure. As these variations are many orders of magnitude smaller than ϵ_t or even ϵ_p , the difficulties are apparent. Fortunately, however, there are many other means of studying theoretically the actions of coöperative phenomena in crystals, some of which I have tried to discuss in this paper.

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

² F. Zwicky, *Ibid.*, **38**, 1772 (1931).

³ F. Zwicky, *Ibid.*, **43**, 270 (1933).

⁴ F. Zwicky, *The Mechanical Engineer*, July issue (1933).⁵ R. Saenger, appearing in the *Phys. Review*.⁶ W. J. de Haas, *Jour. Physique*, 9, 265 (1928).⁷ See F. Zwicky, *Phys. Rev.*, 43, 1031 (1933), where I have given some experimental evidence for the loss of the individuality of electrons.

*CONCENTRATION AND PURIFICATION OF A GROWTH
INHIBITOR EXTRACTED FROM KIDNEY.* A PRELIMINARY
REPORT*

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In a previous paper¹ we described methods for extracting from rat kidneys a substance that inhibited proliferation of renal epithelium. The inhibiting agent was present in acid-alcohol and acid-aqueous extracts of both fresh and desiccated kidney. In the work reported in the present paper there is described the concentration and purification of the inhibitor.

Chemical Methods.—Fresh beef kidneys from older animals were quickly chilled and kept cold until delivered at the laboratory, where they were stripped of capsules and pelvic fibrous and fat tissues. The renal tissue was then passed twice through a meat chopper and at once covered with 0.2 per cent solution of hydrochloric acid in 60 per cent alcohol in the ratio of 500 cc. to 100 gm. of kidney. All of the acid-alcohol was not added at first and the pulp was ground to a finer consistency in a mortar before the entire quantity of acid-alcohol was added. After standing 24 hours at room temperature the acid-alcohol extract was freed of coarse undissolved kidney particles by pouring through cheese-cloth. In the first preparation made from beef kidney this separation was obtained by centrifugation. The volume of filtrate or supernatant alcoholic liquid was then reduced to about 1/30 by fanning. After driving off the alcohol the aqueous residue was brought to the original volume by adding water. This acid extract was neutralized with *N*/1 NaOH using Congo red as an indicator. The neutralization was stopped when a pH of 4.4 to 4.7 was reached. This was judged not only by the color change but also by the character of the precipitate formed. It is essential that the pH be kept below 5. Again if the liquid be too acid it does not clarify perfectly when the acetone is added. An equal volume of pure acetone was added, and the mixture placed in the ice-box overnight. The next day the aqueous acetone extract was filtered through filter paper. The pH of the clear filtrate was taken. It usually was within two points of that of the aqueous solution. The clear extract was fanned down to 1/30 volume to free it of acetone and then made up to the volume of the neutralized aqueous solution by addition of