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Some Properties of Spontaneous Currents

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Summary. The symmetries that admit spontaneous electrical currents are determined. For these symmetries, BLOCH's theorem does not hold. The spontaneous currents do not produce Joule heat; they give rise to a domain structure and to an effect analogous to the Meissner effect. Only 26 magnetic point groups can appear as symmetry groups of a high temperature phase that transforms to a phase admitting spontaneous conduction. Almost all superconductors have heset symmetries. Experiments are proposed that could lead to a deeper understanding of the possible relations between spontaneous conduction and superconductivity.

The quantities that occur in MAXWELL'S equations may be classified according to their behaviour with respect to space inversion I, time reversal R, and the product of both K = IR. The group consisting of these three operations and the identity is the group $\overline{11}'$ (according to the international crystallographic notation) which is isomorphic to the abstract group D_2 . In the following table we classify the charge density, the polarization P, the magnetization M, and the current density j according to the representations of that group¹).

		Т	able 1			
11′	E	Ι	R	K		
A_{g}	1	1	1	1	Q	
B_{σ}	1	-1	1	-1	P_r, P_u, P_z	
A_{μ}^{s}	1	1	-1	-1	$\tilde{M_{r}}, \tilde{M}_{r}, \tilde{M}_{r}$	
B_u^u	1	-1	-1	1	j_x, j_y, j_z	

Out of the 122 crystallographic point groups (called magnetic point groups) that one obtains when time-reversal is included into the list of possible symmetry operations, there are 31 that admit spontaneous currents, i.e. currents that may exist in the absence of an external electric field (see Table 2). More exactly, for each one of these 31 groups, there is at least one component of the current density that transforms with the identity representation.

¹) There exists another classification $(A_g: M_x, M_y, M_z; B_g: j_x, j_y, j_z; A_u: \varrho; B_u: P_x, P_y, P_z)$ compatible with MAXWELL's equations that appears to be unsatisfactory for other reasons.

				15
	Point groups		Direction of spontaneous current	Direction of spontaneous magnetization
1	C_1	1	j	M
2	C_2	2	j_	M_{\star}
3	C,	т	j _r , j _u	$\tilde{M_{z}}$
4	$C_2(C_1)$	2'	j_x, j_y	$\tilde{M_{x}}, M_{y}$
5	$C_{s}(C_{1})$	m'	j,	M_{r}, M
6	$C_i(C_1)$	1'	j	~
7	C_{2n}	mm2	j_z	
8	$D_2(C_2)$	22'2'	$\tilde{j_z}$	M_{z}
9	$C_{2h}(C_2)$	2/m'	$\tilde{j_z}$	
10	$C_{2h}(C_{s})$	2'/m	$\tilde{j_x}, \tilde{j_y}$	
11	$C_{2v}(C_s)$	m'm2'	j_z	M_{1}
12	$D_{2h}(C_{2v})$	mmm'	j_z	8. *
13	C_4	4	j_z	M_{z}
14	$S_4(C_2)$	<u>4</u> ′	j_z	-
15	$C_{4h}(C_4)$	4/m'	j_z	
16	C_{4v}	4mm	$\tilde{j_z}$	
17	$D_4(C_4)$	4 2'2'	j_z	M_z
18	$D_{2d}(C_{2v})$	$\overline{4}'2'm$	j_z	
19	$D_{4h}(C_{4v})$	4/m' m m	j_z	
20	C_3	3	j _z	M_z
21	C_{6}	6	j_z	M_z
22	$C_{3h}(C_{3})$	<u>6</u> ′	j_z	
23	$C_{3i}(C_{3})$	3'	j_z	
24	$C_{6h}(C_6)$	6/m'	j_z	
25	C_{3v}	3m	j_z	
26	$D_{3}(C_{3})$	32'	j_z	M_z
27	$D_{3d} (C_{3v})$	<u>3</u> 'm	j_z	
28	C _{6v}	6 <i>m m</i>	j _z	
29	$D_{6}(C_{6})$	62' 2'	j _z	M_z
30	$D_{3h}\left(C_{3v}\right)$	<u>6</u> 'm 2'	j_z	
31	$D_{6h}(C_{6v})$	6/m' m m	j_z	

Table 2

Eighteen of these groups do not admit of spontaneous magnetization (groups 6, 7, 9, 10, 12, 14, 15, 16, 18, 19, 22, 23, 24, 25, 27, 28, 30, and 31), eight groups admit of spontaneous magnetization parallel to the spontaneous current (groups 2, 8, 13, 17, 20, 21, 26, and 29), three groups would admit of spontaneous magnetization perpendicular to the spontaneous current (groups 3, 5, and 11) and finally for two groups (1 and 4), the angle between the two spontaneous quantities could be arbitrary. The spontaneous current lies in a prescribed plane for three groups (3, 4, and 10); for all other groups, it lies in a prescribed direction.

Two points should be brought into relief:

i) The spontaneous current j does not produce irreversible Joule heat. By hypothesis, the spontaneous current j is not related to any outside field E, therefore the angle between j and E is arbitrary. If j were to produce Joule heat, the rate of change of the entropy density at the absolute temperature T would be $T^{-1} j \cdot E$, and this quantity could be negative as well. Hence either spontaneous currents do not exist

(LANDAU and LIFSHITZ [1]²)) or if they exist as we assume here, they do not produce Joule heat.

ii) BLOCH's famous theorem, according to which 'a system of interacting charged particles in thermal equilibrium has a current density that vanishes everywhere in the absence of external fields' [2] does not apply. This theorem is based on time reversal; however, none of the 31 groups of Table 2 contains the operations of time reversal R.

We shall now find out some characteristic features of spontaneous currents.

The first feature is that the appearance of the state of spontaneous conduction is necessarily accompanied by a change of symmetry at a characteristic temperature. Consequently, a crystal is generally divided into domains. The symmetry of the domains is one of the 31 symmetries of Table 2. In each domain, there flows a spontaneous current. The domains are so oriented that, in the absence of applied fields, the total current through any singly connected section cutting through the crystal vanishes. Like in ferromagnetism, the domain structure may turn out not to be universal[3]. Thus, for instance, in sufficiently small crystals there may be no subdivision into domains. Furthermore, domains in the narrow sense of regions within which the direction of spontaneous current is uniform may not occur if the anisotropy energy $1/2 \Lambda^{ik} j_i j_k$ of the spontaneous currents is low compared to the other energies involved. Here Λ^{ik} is a tensor similar to the London tensor that through $g^i = \Lambda^{ik} j_k$ relates the impulsion g to the density of spontaneous current j [4]. The form of the London tensor for the 31 groups of Table 2 is given in Appendix 1. In any case, it may be said for our model that, below the transition temperature a vector field \mathbf{j}_s is defined throughout the crystal. In the absence of any exterior field the field j_s fulfills at least the following relations:

$$\boldsymbol{j}_s=\mathrm{const.}$$
 , (1)

$$\nabla \cdot \boldsymbol{j}_s = 0$$
 , (2)

$$\boldsymbol{n} \cdot \boldsymbol{j} = 0$$
 . (2')

(*n* is the unit vector normal to the surface of the crystal.) The field j_s satisfying these equations may be piecewise constant or piecewise continuous, or else continuous, depending on the exact physical situation. At the surfaces of discontinuity, the normal component of j_s is continuous.

The second feature is that the distribution of domains as described above leads to a situation where the spontaneous currents flow in closed 'loops'. The size of these loops is neither atomic, nor does it coincide with the dimensions of the specimen; it depends on the size of the domains. The 'diamagnetism' of these loops gives rise to an effect analogous to the Meissner effect. In fact it can be shown that LONDON'S first equation holds for spontaneous currents and that it is closely related to LARMOR'S theorem.

Let us illustrate this for a simple situation. Take a circular loop and a uniform field B perpendicular to the loop. The electrons in the loop acquire an additional angular velocity, the Larmor angular velocity

$$\boldsymbol{\omega}_L = \frac{e}{2 m c} \boldsymbol{B} \qquad (e > 0) \ . \tag{3}$$

²) Numbers in brackets refer to References, page 48.

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The corresponding additional current is

$$\boldsymbol{j}_{L} = -n \ e \ \boldsymbol{v}_{L} = -n \ e \ \boldsymbol{\omega}_{L} \times \boldsymbol{r} = -\frac{n \ e^{2}}{2 \ m \ c} \ \boldsymbol{B} \times \boldsymbol{r} = -\frac{1}{2 \ c} \frac{1}{A} \ \boldsymbol{B} \times \boldsymbol{r}.$$
(4)

 $\Lambda = m/n \ e^2$ is the London-tensor for the isotropic case [5] and r is a vector with origin on the symmetry axis.

Now:

$$c \nabla \times \boldsymbol{j}_L = -\frac{1}{2} \nabla \times (\boldsymbol{B} \times \boldsymbol{r}) = -\boldsymbol{B}$$
 (5)

and this is LONDON'S first equation for the isotropic case.

Thus the proposed model of spontaneously conducting domains seems indeed to imply quite naturally a Meissner effect: when a magnetic field is applied, the current loops react so as to compensate this field in the specimen, by reorientation of the loops and, in particular, by reversal of the spontaneous currents. When all reaction mechanisms have been exhausted, the critical field has been reached. The magnetic field does not exerce its action any more on the current loops, but on the spontaneous currents of the individual domains; the superposition of the symmetry of the field and that of domain generally does not fulfill the necessary conditions for the existence of spontaneous currents. Thus the Meissner effect and the spontaneous currents would disappear simultaneously.

This point of view leads to the conclusion that there is a definite relation between the magnitude of the critical field and the magnitude of the spontaneous currents and that, in particular, the temperature dependence of the critical field reflects the temperature dependence of the spontaneous currents. In the framework of the illustrative formulae (3) to (5), the dependence of the critical field on the spontaneous currents is roughly the following. Generally, we have:

$$\boldsymbol{j}(B) = \boldsymbol{j}_s + \boldsymbol{j}_L(B):$$
(6)

at the critical field \boldsymbol{B}_c

 $j(B_c) = -j_s \,. \tag{7}$

 $j_L(B_c) = 2 j_s$

and

Thus

$$|\boldsymbol{j}_{s}| = \frac{1}{4 c \Lambda} |\boldsymbol{B}_{c}| R$$
(9)

or

$$|\boldsymbol{B}_{c}| = \frac{4 c \Lambda}{R} |\boldsymbol{j}_{s}| .$$

$$(9')$$

Here R is a mean diameter of the loops; a mean already for a single loop that is furthermore averaged over the whole volume.

The change of symmetry here postulated, accompanying the appearance of spontaneous conduction could not be observed, unless the symmetry of a single domain would be determined.

Now it is precisely the postulate that no change of apparent symmetry can be observed at the transition temperature to spontaneous conduction that enables us to find, in a very straightforward manner, the high temperature symmetries that may give rise to a given low temperature symmetry out of those listed in Table 2. The underlying simple rule is the following: the symmetry group of a phase that arises at a

(8)

transition to a state of spontaneous conduction is a 'maximal conductive subgroup' of the symmetry group of the high temperature phase³). By 'conductive subgroup' is meant a subgroup that admits an invariant current density (i.e. one of the groups in Table 2). By 'maximal conductive subgroup' is meant a conductive subgroup that is not contained in any other conductive subgroup. By taking into account the number of times a subgroup appears in a given group[6], one may also determine the various possible orientations of the domains.

In accordance with the requirement of the existence of current loops below the transition temperature, a number of otherwise possible transitions will be excluded in the following. We shall furthermore tentatively exclude symmetries that admit the existence of spontaneous currents and spontaneous magnetization simultaneously. (However, the possibility of such a coexistence should be examined carefully.)

When the procedure outlined above is carried out, it turns out that only 27 magnetic point groups out of the 122 can appear as symmetry groups of the high temperature phase (see Appendix 2). In terms of X-ray symmetry, the result is that compounds must belong, in the high temperature phase, to one of the following eight (ordinary) point groups

$$m m m, 4/m m m, \overline{3} m, \overline{6} m 2, 6/m m m, m 3, 43 m, m 3 m.$$
 (10)

So far as the low temperature symmetry is concerned, some of the 18 groups admitting of spontaneous currents but not admitting of spontaneous magnetization are excluded by the restrictions imposed above. Thus as possible low temperature symmetries remain:

$$2/m'$$
, $m m 2$, $m m m'$, $\overline{4}'$, $4/m'$, $4 m m$, $\overline{4}' 2' m$, $4/m' m m$, $3'$, $3 m$, $\overline{3}' m$. (11)

The same method could of course also be applied to the determination of the space groups admitting of spontaneous currents or transitions to such states.

If now we compare the known high temperature symmetries of superconductors [7] with those listed in (10), it turns out that, with very few exceptions⁴), all superconductors belong to the eight crystal classes (10).

We think that at the present stage of investigation it is not possible to say whether the analogies found between spontaneous currents and superconductivity

³) This rule applies also, with due changes, to ferromagnetism and ferroelectricity, and will be discussed elsewhere.

re:

 crystal class	compounds
 mm 2°)	PtPb ₄ ^a) AuSn ₄ BiPd
6 mm ^c)	Ru ₇ B ₃ , Th ₇ Fe ₃ , Th ₇ Co ₃ , Th ₇ Ni ₃ , Th ₇ Os ₃ , Th ₇ Ir ₃
2/m	Br,Pd
4	Mo_3P^{b})
23	AuBe

a) according to ROESLER et al., Naturw. 38, 331 (1951) the symmetry is D_{4h} ;

^b) according to MATTHIAS et al., Phys. Rev. 93, 1415 (1954) it is not quite certain whether this composition corresponds to a single phase.

c) this symmetry would already admit of spontaneous currents.

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have a deeper physical signification or not. If so, supraconductivity would be linked to specific symmetries.

As it stands, this attempt raises more questions than it answers. The questions raised may however be fruitful ones.

Some of these questions are:

a) At the level of the symmetry of a domain:

- Determination of the symmetries under adequate experimental conditions.

- Verification of the existence of mixed phenomena foreseen by the theory, e.g. 'piezoconductivity' (see Appendix 3).

b) At the level of domain configuration:

- Assessement of LONDON'S second equation within the framework of the theory. LONDON'S second equation seems to be linked in an essential way to the anisotropy of the London tensor Λ^{ik} . Also the Meissner effect and the existence of transport currents appear as antagonistic phenomena. The following two points should help to settle this question.

- Study of the Meissner effect in presence of transport currents.

- Examination of the possibility of existence of superconductive transport currents in a specimen not showing a Meissner effect.

- Determination of the domain configuration, specially its dependence on the inhomogeneities of the specimen. This would help to establish a relation between the various 'kinds' of superconductors and the metallurgical states of the material.

- Observation of the particular properties of crystallites of such a size as to admit only a single domain.

Let us mention finally that a theory of superconductivity in accordance with the point of view expressed in the present outline would not be forced to explain the existence of 'stable wave functions extending over a mile or so of dirty lead wire'[8]; the stability of the wave functions would be required only over the extension of a domain.

An elaboration of the model should include thermodynamic considerations and, as a basis for linking symmetry considerations with existing microscopic theories, a study of the relevant 'magnetic' space groups and their representations.

Appendix 1

The form of the tensor Λ , defined by $g^k = \Lambda^{kl} j_l$, for the 31 groups of Table 2, is the following:

point groups	(Λ^{kl})	
1, ī′	$\begin{pmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{pmatrix}$	a
2, m, 2', m', 2/m', 2'/m	$\begin{pmatrix} 11 & 12 & 0 \\ 12 & 22 & 0 \\ 0 & 0 & 33 \end{pmatrix}$	2 10 11

21	point groups	(Λ^{kl})	e an _a a a a
u R	mm 2, m'm 2', 22'2', mmm'	$\begin{pmatrix} 11 & 0 \\ 0 & 22 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0\\0\\33 \end{pmatrix}$
4 <u>.</u>	4, $\overline{4'}$, $4/m'$, $4 mm$, $42'2'$, $4'2'm$, $4/m'mm$, 3 , 6 , $\overline{6'}$, $\overline{3'}$, $6/m'$, $3 m$, $32'$, $\overline{3'm}$, $6 mm$, $62'2'$, $\overline{6'm2'}$, $6/m'mm$	$\begin{pmatrix} 11 & 0 \\ 0 & 11 \\ 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0\\0\\33 \end{pmatrix}$

Appendix 2

The 27 magnetic point groups that admit transitions to one of the 31 groups of Table 2 under the restrictive conditions discussed in the text.

A STORY CONTRACTOR					
	point groups	II.	(Λ^{lk})	R	
	mmm, m'm'm', mmm1'	0 10	$\begin{pmatrix} 11\\0\\0 \end{pmatrix}$	0 22 0	$\begin{pmatrix} 0\\0\\33 \end{pmatrix}$
	4/mmm, 4/m'm'm', 4'/mmm', 4'/m'm'm, 4/mmm1' 3'm', 3 m 1', 6 m 2, 6 m 21' 6/mmm, 6/m'm'm', 6'/mmm', 6/mmm1'	и S	$\begin{pmatrix} 11\\0\\0 \end{pmatrix}$	$\begin{array}{c} 0\\11\\0\end{array}$	$\begin{pmatrix} 0\\0\\33 \end{pmatrix}$
	m 3, m'3, m 31' 43 m, 4'3 m', 43 m1' m 3 m, m'3 m', m 3 m', m'3 m, m 3 m 1'		$\begin{pmatrix} 11\\0\\0 \end{pmatrix}$	0 11 0	$\begin{pmatrix} 0\\0\\11 \end{pmatrix}$

Appendix 3

The Gibbs function for a domain may be written

$$G = \Lambda^{k} j_{k} + \frac{1}{2} \Lambda^{kl} j_{k} j_{l} + \frac{1}{3} \Lambda^{klm} j_{k} j_{l} j_{m} + \Gamma^{klm} j_{k} x_{lm} + \cdots$$

plus other obvious terms such as $\alpha^{ik} E_i j_k$ and $\beta^{ik} H_i j_k$ that we shall not discuss here. x_{lmlm} is the stress tensor. In consequence, the relation between the impulsion g and the spontaneous current j is

$$\frac{\partial G}{\partial j_k} = g^k = \Lambda^k + \Lambda^{k\,l}\,j_l + \Lambda^{k\,l\,m}\,j_l\,j_m + \Gamma^{k\,l\,m}\,x_{l\,m} + \cdots$$

This equation is a generalization of the Laue equation $g^k = \Lambda^{kl} j_l$ that we mentioned previously. The term $\Gamma^{klm} x_{lm}$ represents a phenomenon analogous to piezo-electricity and piezomagnetism, and may be called piezoconductivity.

There are 66 point groups admitting of 16 types of piezoconductive tensors as shown in the following table. (The conventional notation for the strain tensor with one index running from one to six is utilized.) Vol. 39, 1966

	point groups		Г						
1	1, 1'		11 21 31	12 22 32	13 23 33	14 24 34	15 25 35	16 26 36)
2	2, m', 2/m'		0 0 31	0 0 32	0 0 33	14 24 0	15 25 0	0 0 36)
3	m, 2', 2'/m	(11 21 0	12 22 0	13 23 0	0 0 34	0 0 35	16 26 0)
4	222, m'm'2, m'm'm'		0 0 0	0 0 0	0 0 0	14 0 0	0 25 0	0 0 36	.)
5	mm2, 22'2', m'm2', mmm'		0 0 31	0 0 32	0 0 33	0 24 0	15 0 0	0 0 0)
6	4, 4 ′, 4/m′, 6, 6 ′, 6/m′	Ć	0 0 31	0 0 31	0 0 33	14 15 0	$ \begin{array}{r} 15 \\ -14 \\ 0 \end{array} $, 0 0 0)
7	4, 4', 4'/m'		0 0 31	$0 \\ 0 \\ -31$	0 0 0	$ \begin{array}{r} 14 \\ -15 \\ 0 \end{array} $	15 14 0	0 0 36)
8	422, 4'2m', 4m'm', 4/m'm'm', 622, 6'm'2, 6m'm', 6/m'm'm'		0 0 0	0 0 0	0 0 0	14 0 0	$ \begin{array}{r} 0 \\ -14 \\ 0 \end{array} $	0 0 0)
9	42m, 4'22', 42'm', 4'mm', 4' m'm'm	(0 0 0	0 0 0	0 0 0	14 0 0	0 14 0	0 0 36)
10	4mm, 42'2', 4 '2'm, 4 m'mm, 6mm, 62'2', 6 'm2', 6 m'mm		0 0 31	0 0 31	0 0 33	$\begin{array}{c} 0\\ 15\\ 0\end{array}$	15 0 0	0 0 0)
11	3, 3′	(-	11 - 22 31	$-11 \\ 22 \\ 31$	0 0 33	14 15 0	$ \begin{array}{r} 15 \\ -14 \\ 0 \end{array} $	-2(2) -2(1) 0	$\begin{array}{c} 2) \\ 1) \end{array} \right)$
12	32, 3m', 3'm'	(-	0 - 22 0	0 22 0	0 0 0	14 0 0	$\begin{array}{c} 0\\ -14\\ 0\end{array}$	-2(2) 0 0	2)
13	3m, 32', 3'm		11 0 31	$-11 \\ 0 \\ 31$	0 0 33	0 15 0	15 0 0	$- \begin{array}{c} 0 \\ 2(1) \\ 0 \end{array}$	1))
14	ō, 6', 6' m	(-	11 - 22 0	-11 22 0	0 0 0	0 0 0	0 0 0	-2(2) -2(1) 0	$\begin{pmatrix} 2)\\ 1 \end{pmatrix}$

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	point groups		Г						
15	Бт2, 6'22', Бт'2', 6'тт' 6' ттт'	(_	0	0 22	0	0	0	- 2(2 0)	²⁾
	S Immin		0	0	0	0	0	0)
16	23, m'3, 4 3m, 4'32', m'3m	(0	0	0	14	0 14	0)
			0	0	0	0	0	14)

Among these, there are, of course, the 31 point groups of Table 2; the remaining 35 point groups are capable of piezoconductivity but not of spontaneous conduction. Among the 26 high-temperature phases listed in appendix 2, only the following 10 admit of piezoconductivity: m'm'm', 4/m'm'm', 4'/m'm'm, $\bar{3}'m'$, $\bar{6}m2$, 6/m'm'm', 6'/mmm', m'3, $\bar{4}3m$, m'3m.

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