The radial distortions induced by a pure electrostatic field always meet this second requirement.

The $G^4(4f,m_l';p,m_l)$ terms act in much the same way, i.e.,

$$\Delta' = -\frac{1}{189}[16G^4(p,0)+20G^4(p,\pm1)] = \text{const}+\frac{4}{189}\delta_4;\quad m_l'=0,$$

$$\Delta' = -\frac{1}{189}[15G^4(p,0)+21G^4(p,\pm1)] = \text{const}+\frac{3}{189}\delta_4;\quad m_l'=\pm1,$$

$$\Delta' = -\frac{1}{189}[12G^4(p,0)+24G^4(p,\pm1)] = \text{const}+0\delta_4;\quad m_l'=\pm2,$$

$$\Delta' = -\frac{1}{189}[7G^4(p,0)+29G^4(p,\pm1)] = \text{const}-\frac{5}{189}\delta_4;\quad m_l'=\pm3, \tag{A6}$$

where here

$$\text{const} = \frac{36}{189}G^4(p,0)+\frac{24}{189}\delta_4, \tag{A7}$$

so again we have linear shielding. Such behavior does not occur for the d-shell exchange terms.

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Reversal in Optical Rotatory Power—"Gyroelectric" Crystals and "Hypergyroelectric" Crystals

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A crystal is provisionally referred to as being "gyroelectric," when its optical rotatory power or gyration is nonzero at no biasing electric field and can be reversed in sign by means of a suitable biasing electric field. The gyroelectric crystals must be ferroelectric. It is found that, of the 19 kinds of regular ferroelectrics, only 9 kinds are gyroelectric. It is further shown that the other 10 kinds are divided into 5 "hypergyroelectric" and 5 optically inactive kinds. The rate of change of the gyration with the biasing electric field at zero value of the biasing electric field is provisionally referred to as the "electrogyration." The hypergyroelectric crystals are, somewhat roughly speaking, those crystals whose electrogyration is nonzero and can be reversed in sign by means of a suitable biasing electric field. Also, as a first step in the investigation of the properties of the gyroelectric and hypergyroelectric crystals, a theoretical inference is made into the change with temperature T of the gyration G_s at no biasing field and electrogyration η of the gyroelectric and hypergyroelectric crystals in the neighborhood of their Curie temperature T_0. On some assumptions, the following are presumed. In the gyroelectrics, G_s changes like $(T_0-T)^{1/2}$ with T below T_0 and vanishes above T_0. In the hypergyroelectrics, G_s changes linearly with T both below and above T_0, but breaks at T_0. In the gyroelectrics, η changes like $(T_0-T)^{-1}$ below T_0 and changes like $2(T-T_0)^{-1}$ above T_0. In the hypergyroelectrics, η changes like $(T_0-T)^{-1/2}$ below T_0 and vanishes above T_0.

1. INTRODUCTION

We provisionally refer to the crystals as being "gyroelectric" whose optical rotatory power or gyration[1] is nonzero at no biasing electric field and can be reversed in sign by means of a suitable biasing electric field. (A crystal which has a nonzero gyration is also called optically active. The reason why the term "biasing electric field" is used in place of the simpler term "electric field" lies in the distinction of it from the "electric field" of the light.) From this definition it may be obvious that the gyroelectric crystals must be ferroelectric. (A most reasonable and exact definition of ferroelectricity has been given in the preceding papers.[2,3]) In general, the ferroelectric crystals are divisible into the *regular* ferroelectric crystals and the *irregular* ones.[2,3] We refer to those gyroelectric crystals which are regularly ferroelectric as the regular gyroelectric crystals.

In this paper the gyroelectric crystals considered are limited to the regular ones. In Sec. 2, a determination is made as to which of the regular ferroelectric crystals should be gyroelectric. On this occasion it will be shown that the regular ferroelectric crystals consist of the gyroelectric, the "hypergyroelectric," and the optically inactive crystals. The rate of change of the gyration with the biasing electric field at zero value of the biasing electric field is provisionally referred to as the "electro-

[1] See, for example, J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, England, 1957).

[2] K. Aizu, Rev. Mod. Phys. 34, 550 (1962).

[3] K. Aizu, Phys. Rev. 133, A1350 (1964).

gyration." The hypergyroelectric crystals are, somewhat roughly speaking, those crystals whose electrogyration is nonzero and can be reversed in sign by means of a suitable biasing electric field. This definition of hypergyroelectricity is not exact. For, the electrogyration depends on not only the direction of the light but also the direction of the infinitesimal biasing electric field, relative to the crystal; the above definition makes no reference to this fact. The exact definition is given in Sec. 2.

In Sec. 3, as a first step in the investigation of the properties of the gyroelectric and hypergyroelectric crystals, a theoretical inference is made into the variation with temperature of the gyrations and electrogyrations of the regular gyroelectric and hypergyroelectric crystals in the neighborhood of their Curie temperatures. The method is an extension of Devonshire's method[4] in the phenomenological theory of ferroelectricity.

Gyroelectricity and hypergyroelectricity seem to be of interest not only theoretically or experimentally but also from the practical point of view. The researches on these phenomena are, however, only recent, and not many have been reported up to now.[5,6] There are analogies between gyroelectricity and ferroelectricity. The gyration at no biasing electric field corresponds to the spontaneous polarization. The reversal in the gyration corresponds to the reversal in the spontaneous polarization. The electrogyration corresponds to the dielectric susceptibility. Just as many of the ferroelectric crystals have a large dielectric susceptibility, many of the gyroelectric crystals are expected to have a large electrogyration. What correspond to the hypergyroelectric crystals would be the "hyperferroelectric" crystals whose dielectric susceptibility is nonzero and can be reversed in sign by means of a suitable electric field. These crystals are, however, nonexistent, as is theoretically evident. Many of the hypergyroelectric crystals are also expected to have a large electrogyration.

2. REGULAR GYROELECTRIC CRYSTALS AND REGULAR HYPERGYROELECTRIC CRYSTALS

The gyration G depends on the direction of the light relative to the crystal in the form[1]

$$G=\tilde{G}:\mathbf{nn}=\sum_{i=1}^{3}\sum_{j=1}^{3}G_{ij}n_in_j,$$

where $\tilde{G}$ is the gyration tensor of the crystal, whose components are G_{ij}, and $\mathbf{n}$ is the wave-normal unit vector of the (plane wave) light, whose components are n_i. The gyration tensor is a symmetric axial tensor of rank two.

Previously,[2,3] it has been shown that the regular ferroelectrics are divisible into 19 kinds in accordance with their point groups, Bravais lattices, and types of state transition (or polarization reversal), and that the matrical form in one state, and the manner of change with the state transition, of a tensorial property of the regular ferroelectrics are uniquely determinate to each of the 19 kinds. These 19 kinds have been denoted by[3]

*r*1, *rm*, *r*2, *rmm*2, *r*4-I, *r*4-II, *r*4*mm*,
*r*6-I, *r*6-II, *r*6*mm*, *r*3*R*-I, *r*3*R*-II, *r*3*mR*,
*r*3*P*-I, *r*3*P*-II, *r*3*P*-III, *r*3*P*-IV, *r*3*mP*-I, *r*3*mP*-II.

According to Sec. 3.3 of Ref. 3, the following are found. The gyration tensor is zero for the five kinds

*r*4*mm*, *r*6*mm*, *r*3*mR*, *r*3*mP*-I, *r*3*mP*-II;

it is nonzero and unchanged by the state transition for the five kinds

*r*4-II, *r*6-II, *r*3*R*-II, *r*3*P*-III, *r*3*P*-IV;

it is nonzero and reversed in sign by the state transition for the nine kinds

*r*1, *rm*, *r*2, *rmm*2, *r*4-I, *r*6-I, *r*3*R*-I, *r*3*P*-I, *r*3*P*-II.

Therefore, we see that the first 5 kinds are optically inactive and, of course, not gyroelectric, the second 5 kinds are optically active but not gyroelectric, and the last 9 kinds are just gyroelectric. Thus, eventually, it turns out that the regular gyroelectric crystals are the last 9 kinds of regular ferroelectrics.

We provisionally refer as the "electrogyration tensor" to the tensor $\tilde{\eta}$ equal to the rate of change of the gyration tensor $\tilde{G}$ with the biasing electric field vector $\mathbf{E}$ at $\mathbf{E}=0$:

$$\tilde{\eta}\equiv(\partial\tilde{G}/\partial\mathbf{E})_{\mathbf{E}=0}\quad\text{or}\quad\eta_{ijk}\equiv(\partial Gg_{ij}/\partial E_k)_{\mathbf{E}=0}.$$

Since $G_{ij}=G_{ji}$, the equality

$$\eta_{ijk}=\eta_{jik}$$

holds. The electrogyration tensor is thus a partially symmetric axial tensor of rank three. In Sec. 1 the electrogyration η has been defined as

$$\eta\equiv(\partial G/\partial E)_{E=0};$$

in this case the biasing electric field E is applied in a fixed direction, which we denote by $\mathbf{b}$ (unit vector). As can easily be proved, η is connected with $\tilde{\eta}$ as

$$\eta=\tilde{\eta}\vdots\mathbf{nnb}=\sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\eta_{ijk}n_in_jb_k.$$

This equation explicitly shows the dependence of the electrogyration upon the directions of the light and of the infinitesimal biasing field.

In the regular ferroelectrics the case is the most important where the biasing field is applied in the direction of the spontaneous polarization vector. (As for

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[4] A. Devonshire, Advan. Phys. 3, 85 (1954).
[5] H. Futama and R. Pepinsky, J. Phys. Soc. Japan 17, 725 (1962).
[6] J. Kobayashi and N. Yamada, J. Phys. Soc. Japan 17, 876 (1962).

sense, the biasing field is not necessarily the same as the spontaneous polarization vector.) In this case, if the direction of the spontaneous polarization vector is denoted by **c** (unit vector), then

$$\eta=\tilde{\eta}^\circ:\mathbf{nn}=\sum_{i=1}^{3}\sum_{j=1}^{3}\eta^\circ{}_{ij}n_in_j,$$

$$\tilde{\eta}^\circ\equiv\tilde{\eta}\cdot\mathbf{c}\quad\text{or}\quad\eta^\circ{}_{ij}\equiv\sum_{k=1}^{3}\eta_{ijk}c_k.$$

(We take **c** independent of the state transition. Therefore, **c** does not necessarily agree in sense with the spontaneous polarization vector.) The component tensor $\tilde{\eta}^\circ$ of the electrogyration tensor in the direction of the spontaneous polarization vector is a symmetric axial tensor of rank two, as $\tilde{G}$ is. It is seen that the relation between η and $\tilde{\eta}^\circ$ is the same as that between G and $\tilde{G}$.

According to Sec. 3.5 of Ref. 3, the following are found. The tensor $\tilde{\eta}^\circ$ is zero for all the optically inactive kinds; it is nonzero and reversed in sign by the state transition for all the optically active but nongyroelectric kinds; it is nonzero and unchanged by the state transition for all the gyroelectric kinds. Thus, it turns out that $\tilde{\eta}^\circ$ is another quantity that clearly distinguishes between the optically inactive, the optically active but nongyroelectric, and the gyroelectric kinds. ($\tilde{\eta}^\circ$ does not behave for the state transition in the same manner as $\tilde{G}$ does because **c** is free in sense from the crystal.) We refer to the optically active but nongyroelectric kinds as being "hypergyroelectric," with our interest in the above property of theirs, that the component tensor of the electrogyration tensor in the direction of the spontaneous polarization vector is nonzero and reversed in sign by the state transition, or that the electrogyration is nonzero and can be reversed in sign by means of a suitable biasing electric field. (The latter statement is plainer but somewhat rough.)

The kind *r3P*-II is singular among the gyroelectric kinds, and the kind *r3mP*-II is singular among the optically inactive kinds; for, the electrogyration tensor is unchanged by the state transition for all the other gyroelectric and all the other optically inactive kinds, but not for the kinds *r3P*-II and *r3mP*-II.[3] (The electrogyration tensor is nonzero in all kinds of regular ferroelectrics.) When the z axis is taken parallel to the spontaneous polarization vector, the electrogyration is

$$\eta=\eta_{111}n_1^2+2\eta_{121}n_1n_2+\eta_{221}n_2^2$$

for the infinitesimal biasing field applied in the x direction and for the light with the wave-normal perpendicular to the z axis. In the kinds *r3P*-II and *r3mP*-II, this electrogyration η is reversed in sign by the state transition, since η_{111}, η_{121}, and η_{221} are reversed in sign by the state transition.[3]

It should not be taken that in the hypergyroelectric crystals the electrogyration is reversed in sign by the state transition for *all* directions of the infinitesimal biasing field and for *all* directions of the light. (As a matter of course, when the infinitesimal biasing field is applied parallel to the spontaneous polarization vector, the electrogyration is reversed in sign by the state transition for *all* directions of the light.) Let us consider, for example, a hypergyroelectric crystal of the kind *r4*-II. If the z axis is taken parallel to the spontaneous polarization vector, the electrogyration is

$$\eta=2\eta_{231}n_2n_3$$

for the infinitesimal biasing field applied in the x direction and for the light with the wave-normal perpendicular to the x axis. This electrogyration η is unchanged by the state transition, since η_{231} is unchanged by the state transition.[3] It is noted that any hypergyroelectric kind is only of rotation type and not of inversion type nor of reflection type.[2,3]

3. TEMPERATURE DEPENDENCE OF THE GYRATION AND ELECTROGYRATION IN THE GYROELECTRIC AND HYPERGYROELECTRIC CRYSTALS

In this section we make a theoretical inference into the question how the gyration and electrogyration of the regular gyroelectric and hypergyroelectric crystals should vary with the temperature in the neighborhood of their Curie temperature. For simplicity it is assumed that the biasing electric field is applied along the unique axis of the crystals, and that the wave-normal of the light is parallel or perpendicular to the unique axis. As is well known, the direction of the spontaneous polarization vector agrees with that of the unique axis in all kinds except *r*1 and *rm*. In the kinds *r*1 and *rm*, the direction of the spontaneous polarization vector is variable with temperature. We exclude these two kinds from our consideration.

Once Devonshire[4] assumed that the free energy ϕ of the ferroelectrics is expressible in the form

$$\phi=\phi_0+A(T-T_0)P^2+\sum_{n=2}^{\infty}B_nP^{2n},\tag{1}$$

where P is the polarization, T the temperature, ϕ_0 a function of T alone, A a positive constant, T_0 a positive constant, and B_n a constant which is zero for all larger than a certain value of n. On this assumption he could qualitatively explain several phenomena characteristic of the ferroelectrics.

We assume, in addition to (1), that the gyration G of the gyroelectric and hypergyroelectric crystals is expressible in the form

$$G=\alpha+\beta(T-T_0)+\sum_{n=1}^{\infty}\gamma_nP^n,\tag{2}$$

where α and β are constants and γ_n is a constant which is zero for all larger than a certain value of n. The simplest form of explicit dependence of G upon T is such

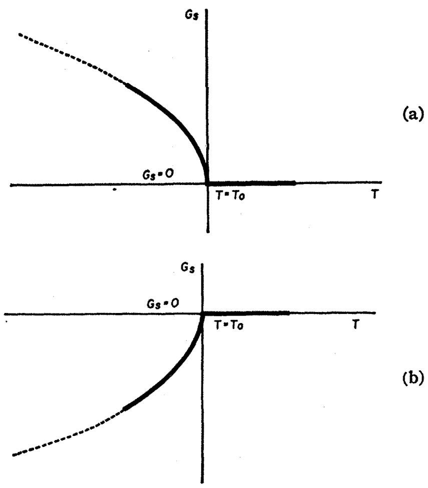

FIG. 1. Temperature dependence of the gyration G_s in the gyroelectrics. (a) is for the case of $\gamma_1>0$; (b) is for the case of $\gamma_1<0$.

that all γ_n, including γ_0, are independent of T. The next simplest form is (2) in which only γ_0 depends on T and that linearly. Assumption of a complicated form is meaningless since it has been assumed that the form of explicit dependence of ϕ upon T is a simple form of (1).

The sign of B_2 is important. If $B_2>0$, the phase transition at the Curie temperature T_c is of second order and $T_c=T_0$; if $B_2<0$, the phase transition at T_c is of first order and $T_c\neq T_0$.[4] In the present paper we consider only the former case; the argument in the latter case is somewhat harder but similar. In the case of $B_2>0$, Devonshire[4] assumed

$$B_n=0 \quad \text{for} \quad n>2,$$

or

$$\phi=\phi_0+A(T-T_0)P^2+B_2P^4. \tag{3}$$

We assume, in addition to (3),

$$\gamma_n=0 \quad \text{for} \quad n>2,$$

or

$$G=\alpha+\beta(T-T_0)+\gamma_1P+\gamma_2P^2. \tag{4}$$

It is anticipated that the values of α, β, γ_1, and γ_2 may depend considerably on the direction of the light.

From the definitions of gyroelectricity and hypergyroelectricity, it is evident that the gyration G must be odd with respect to P for the gyroelectrics and even with respect to P for the hypergyroelectrics. Therefore, in (4), it must hold that

$$\alpha=\beta=\gamma_2=0$$

or

$$G=\gamma_1P \tag{5}$$

for the gyroelectrics, and

$$\gamma_1=0$$

or

$$G=\alpha+\beta(T-T_0)+\gamma_2P^2 \tag{6}$$

for the hypergyroelectrics.

The temperature dependence of the spontaneous polarization P_s is derived from (3) as[4]

$$\begin{aligned} P_s&=(A/2B_2)^{1/2}(T_0-T)^{1/2} \quad &\text{for} \quad T\leqq T_0 \\ &=0 &\text{for} \quad T\geqq T_0. \end{aligned} \tag{7}$$

The temperature dependence of the gyration G_s at no biasing fields is obtained, by substituting (7) into (5)

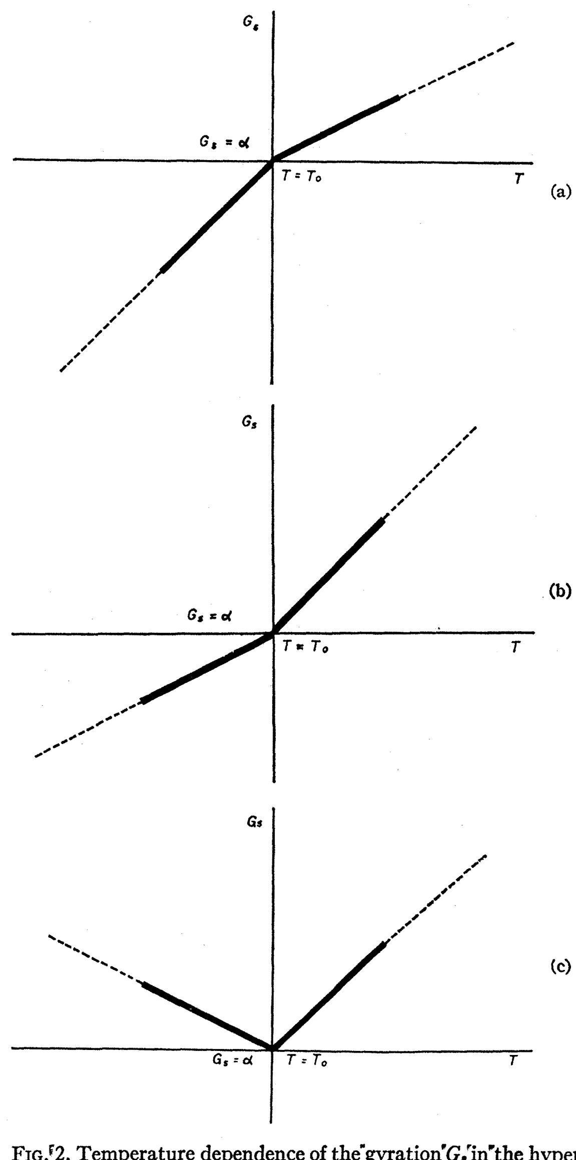

FIG. 2. Temperature dependence of the gyration G_s in the hypergyroelectrics. It is assumed that $\beta>0$. (a), (b), and (c) are for the cases of $\gamma_2<0$, $0<\gamma_2<2\beta B_2/A$, and $\gamma_2>2\beta B_2/A$, respectively. It should be noted that the cross point of the abscissa with the ordinate is (T_0,α) and not $(T_0,0)$.

and (6), as

$$G_s=\gamma_1(A/2B_2)^{1/2}(T_0-T)^{1/2} \quad \text{for} \quad T\leqq T_0$$
$$=0 \quad \text{for} \quad T\geqq T_0, \tag{8}$$

for the gyroelectrics, and

$$G_s=\alpha+(\gamma_2 A/2B_2-\beta)(T_0-T) \quad \text{for} \quad T\leqq T_0$$
$$=\alpha+\beta(T-T_0) \quad \text{for} \quad T\geqq T_0, \tag{9}$$

for the hypergyroelectrics.

Differentiating (5) and (6) with respect to the biasing field E and then putting $E=0$, we have

$$\eta=\gamma_1\chi, \tag{10}$$

for the gyroelectrics, and

$$\eta=2\gamma_2 P_s\chi, \tag{11}$$

for the hypergyroelectrics. Here, η and χ are the electrogyration and the dielectric susceptibility, respectively. The temperature dependence of χ is derived from (3) as[4]

$$\chi^{-1}=4A(T_0-T) \quad \text{for} \quad T<T_0$$
$$=2A(T-T_0) \quad \text{for} \quad T>T_0. \tag{12}$$

The temperature dependence of η is obtained, by substituting (7) and (12) into (10) and (11), as

$$\eta=(\gamma_1/4A)(T_0-T)^{-1} \quad \text{for} \quad T<T_0$$
$$=(\gamma_1/2A)(T-T_0)^{-1} \quad \text{for} \quad T>T_0, \tag{13}$$

for the gyroelectrics, and

$$\eta=\gamma_2(8AB_2)^{-1/2}(T_0-T)^{-1/2} \quad \text{for} \quad T<T_0$$
$$=0 \quad \text{for} \quad T>T_0, \tag{14}$$

for the hypergyroelectrics.

Equations (8), (9), (13), and (14) are graphed in Figs. 1, 2, 3, and 4, respectively. At present, no experiment is reported on the temperature dependence of G_s and η in the neighborhood of the Curie temperature. It is expected that our results would be compared with experimental observations.

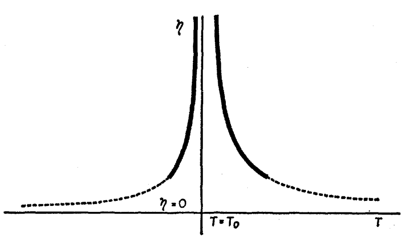

FIG. 3. Temperature dependence of the electrogyration η in the gyroelectrics. It is assumed that $\gamma_1>0$.

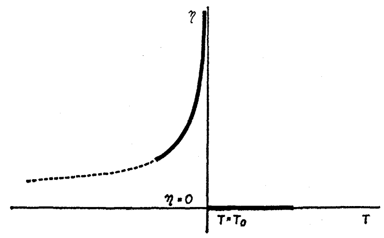

FIG. 4. Temperature dependence of the electrogyration η in the hypergyroelectrics. It is assumed that $\gamma_2>0$.

A commentary is necessary upon the gyroelectrics of the kind $rmm2$. In these crystals, if the z axis is taken parallel to the diad axis of symmetry and the x axis perpendicular to one of the mirror planes of symmetry, the dependence of G_s upon the direction $\mathbf{n}$ of the light is given by[3]

$$G_s=2G_{12}n_1n_2.$$

Therefore, G_s must be zero for the lights propagating along the x, y, and z axes, and hence, according to (8), γ_1 must be zero for those lights. Figures 1 and 3 are not available for the case of $\gamma_1=0$.

4. CONCLUSIONS

Of the 19 kinds of regular ferroelectrics, the 9 kinds

*r*1, *rm*, *r*2, *rmm*2, *r*4-I, *r*6-I, *r*3*R*-I, *r*3*P*-I, *r*3*P*-II

are gyroelectric, the 5 kinds

*r*4-II, *r*6-II, *r*3*R*-II, *r*3*P*-III, *r*3*P*-IV

are hypergyroelectric, and the 5 kinds

*r*4*mm*, *r*6*mm*, *r*3*mR*, *r*3*mP*-I, *r*3*mP*-II

are optically inactive.

The gyration at no biasing electric field G_s and the electrogyration η of the gyroelectric and of the hypergyroelectric crystals are presumed to vary with the temperature T in the neighborhood of the Curie temperature T_0 in manners as follows. In the gyroelectrics, G_s varies like $(T_0-T)^{1/2}$ with T below T_0 and vanishes above T_0. In the hypergyroelectrics, G_s varies linearly with T both below and above T_0, but breaks at T_0. In the gyroelectrics, η varies like $(T_0-T)^{-1}$ below T_0 and varies like $2(T-T_0)^{-1}$ above T_0. In the hypergyroelectrics, η varies like $(T_0-T)^{-1/2}$ below T_0 and vanishes above T_0.

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