Determination of the Kind for Actual Ferroelectrics, Together with Examination of the Characters of Their Paraelectric Phase Transformations

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It was shown that the ferroelectrics are divisible into 30 kinds in accordance with their point groups, Bravais lattices, and types of state transition; 19 of these 30 kinds are regular and the remaining 11 are irregular. In this paper, the determination of the kind is attempted for the actual ferroelectrics discovered up to now. Some useful methods for this purpose are explained. It is confirmed that every actual ferroelectric does belong to one of the 30 kinds. On the other hand, it is seen that, at the present stage, not all of the 30 kinds have actual ferroelectrics belonging to them. Incidentally, an examination is made of the characters of the paraelectric phase transformations of actual ferroelectrics. It is found that only the barium titanate family and the methylammonium aluminum sulfate dodecahydrate family (and possibly the ammonium cadmium sulfate family) have a complex phase transformation, and all the others a primitive phase transformation. (The ferroelectrics having no paraelectric phase transformation are excluded.) Among the kinds not occupied by any actual ferroelectric, the kinds i1-I, i1-II, and im are singular, because ferroelectrics belonging to them, if any, should change to paraelectrics of polar point groups by a primitive phase transformation. A suggestion is made of a way of discovering such ferroelectrics. The present work also serves for finding gyroelectrics and hypergyroelectrics among known ferroelectrics.

1. INTRODUCTION

WE recognize "ferroelectricity" as the following[1-4]: When a crystal plate, in some direction, of a crystal has two stable states at zero electric field, and is capable of alternating between these states by means of an electric field, the crystal plate or the crystal is said to be ferroelectric. Here, the two stable states are assumed to be identical or enantiomorphous in crystal structure and to be equal in plate thickness. Since the state transition is to be brought about by an electric field, it is natural that the two stable states should be different in polarization.

We divided all ferroelectrics into *regular* ferroelectrics and *irregular* ferroelectrics.[1-4] A ferroelectric crystal is said to be regular[1] when (1) in any crystal plate with any Miller indices of the crystal, the space lattice in one of the two stable states is parallel to the space lattice in the other, and (2) the notion of the two stable states is possible, not only for the individual crystal plates, but for the crystal as a whole. It can also be restated that the regular ferroelectrics are those ferroelectrics which belong to the polar point groups and satisfy the first condition for regularity, i.e., the condition of lattice parallelism. The irregular ferroelectrics are the ferroelectrics which are not regular.

In this paper, as in the preceding papers,[3,4] we leave the ferroelectrics belonging to the nonpolar (but non-centrosymmetrical) groups out of consideration; these ferroelectrics are hardly expected to exist,[1] and, in fact, none have yet been discovered.

It was shown[1,3] that the regular ferroelectrics and the irregular ferroelectrics are divisible into 19 kinds and 11 kinds, respectively, in accordance with their point groups, Bravais lattices, and types of state transition. Thus, all the ferroelectrics (belonging to the polar groups) are divisible into 30 kinds. We denoted[2,3] the 19 regular kinds by the symbols

$$r1, \; rm, \; r2, \; rmm2, \; r4\text{-I}, \; r4\text{-II}, \; r4mm,$$
$$r6\text{-I}, \; r6\text{-II}, \; r6mm, \; r3R\text{-I}, \; r3R\text{-II}, \; r3mR,$$
$$r3P\text{-I}, \; r3P\text{-II}, \; r3P\text{-III}, \; r3P\text{-IV},$$
$$r3mP\text{-I}, \; r3mP\text{-II},$$

and the 11 irregular kinds by the symbols

$$i1\text{-I}, \; i1\text{-II}, \; im, \; i2\text{-I}, \; i2\text{-II}, \; imm2,$$
$$i4, \; i6, \; i3R, \; i3P\text{-I}, \; i3P\text{-II}.$$

When ferroelectrics undergo the state transition, their tensorial properties are changed in a manner unique and definite for each of the 30 kinds. In Refs. 2 and 3, these manners of change were determined systematically for the polar and axial tensors of ranks two, three, and four.

In Ref. 4, we investigated the problem of symmetries in the paraelectric phase transformations of ferroelectric crystals. (By "the paraelectric phase transformation of a ferroelectric crystal" we mean[4] "the phase transformation of a ferroelectric crystal to a paraelectric phase," and by "the ferroelectric phase transformation of a paraelectric crystal" we mean "the phase transformation of a paraelectric crystal to a ferroelectric phase." Some authors seem to use for both concepts the same term "the ferroelectric phase transformation.") As we know,[1,3] one of the two stable states of a ferroelectric is obtained by performing upon the other any of certain operations (referred to as **F** operations) belonging to the rotation group. We referred[4] to a paraelectric phase transformation of a ferroelectric crystal as being *primitive* or *complex*, respectively, when the symmetry elements of the paraelectric phase comprise the symmetry

[1] K. Aizu, Rev. Mod. Phys. **34**, 550 (1962).
[2] K. Aizu, Phys. Rev. **133**, A1350 (1964).
[3] K. Aizu, Phys. Rev. **134**, A701 (1964).
[4] K. Aizu, J. Phys. Soc. Japan **19**, 918 (1964).

elements of the ferroelectric phase and the **F** operations
alone, or when they include some other extra symmetry
elements in addition.

The primitive phase transformations are the smooth-
est ones of all conceivable paraelectric phase transfor-
mations of ferroelectric crystals. The complex phase
transformations are the next smoothest. It is expected
that the paraelectric phase transformation of an arbi-
trary ferroelectric crystal very probably is primitive. It
is also expected that paraelectric phase transformations
that are neither primitive nor complex are exceptional.
Let us suppose that a ferroelectric having a paraelectric
phase transformation is subjected to an electric field
oblique to its unique ferroelectric direction in the vi-
cinity of its Curie temperature. Then, if the phase
transformation is complex, there may arise new domains
with the unique ferroelectric direction different from
the original one; if the phase transformation is primitive,
no such domains may arise. Let us also suppose that a
sample, consisting of a single domain, of a ferroelectric
having a paraelectric phase transformation is once taken
to the paraelectric phase and then returned to the ferro-
electric phase by varying the temperature at zero
electric field. Then, if the phase transformation is com-
plex, there may arise not only 180° domains but also
more complicated domains, such as 90° domains and
109 and 71° domains; if the phase transformation is
primitive, only 180° domains may arise. (For a fuller
explanation, see Ref. 4.)

For the ferroelectrics having a primitive phase trans-
formation, we presented[4] tables that give the point
group (or the space group) of the paraelectric phase
when the kind alone (or both the kind and space group)
of the ferroelectrics is specified.

In the present paper, we attempt to determine the
kind for the acutal ferroelectrics discovered up to now.
If one knows the **F** operations or the kind of a ferro-
electric, one can deduce the (macroscopic and micro-
scopic) characteristics of the ferroelectric in one state
from the information about the other state, and more-
over, can make some predictions on the paraelectric
phase transformation of the ferroelectric. For ferro-
electrics, specification of the kind is much more infor-
mative than specification of the point group; the former
involves the latter.

The point groups $4mm$ and $6mm$ and the point group
$3m$ with the trigonal R lattice comprise only one kind
each; these kinds are $r4mm$, $r6mm$, and $r3mR$, re-
spectively. For these point groups, therefore, the de-
termination of the kind is no particular problem.

All the other polar point groups (including the point
group $3m$ with the hexagonal P lattice) are divided into
two or more kinds each; for example, the point group
2 is divided into three kinds $r2$, $i2$-I, and $i2$-II. There
are various methods of determining the kind for these
point groups. The most convenient ones, however, may
be the following three. One is to examine the symmetry
change in the paraelectric phase transformation, as

proposed in Ref. 4. Another is to observe the ferro-
electric transformations of tensorial properties, as pro-
posed in Refs. 2 and 3. The third is to compare the
orientations of the space lattices in the two stable states.

Although the first method is unusable for the ferro-
electrics having no paraelectric phase transformation,
it is, in practice, very useful, because many of the actual
ferroelectrics have such a phase transformation, and
because for almost all of them the space group or point
group of the paraelectric phase is known. This method
is, however, incapable of distinguishing the kinds

$$i4,\ i6,\ i3R,\ i3P\text{-I},\ i3P\text{-II} \qquad\qquad \text{(a)}$$

from the kinds

$$r4\text{-II},\ r6\text{-II},\ r3R\text{-II},\ r3P\text{-III},\ r3P\text{-IV}, \qquad \text{(b)}$$

respectively.

The second method is usable for all ferroelectrics, and,
in particular, important for the ferroelectrics having no
paraelectric phase transformation. At present, however,
it is not so useful because there are only a small number
of experimental data on the ferroelectric transformations
of tensorial properties.

The third method is capable of distinguishing between
a regular kind and an irregular kind and between an
irregular kind and another irregular kind, but not be-
tween a regular kind and another regular kind. For
example, let us consider a ferroelectric belonging to
point group 2. We inspect the crystal plate of this
ferroelectric perpendicular to the diad axis of symmetry.
The kind of this ferroelectric can be concluded to be
$r2$, $i2$-I, or $i2$-II, according to whether the space lattice
in one of the two stable states is parallel to the space
lattice in the other, or such as is obtained by rotating
the space lattice in the other by 90° about the diad axis
of symmetry, or such as is obtained by reflecting the
space lattice in the other across a plane parallel to the
diad axis of symmetry. (The kinds $i3P$-I and $i3P$-II
cannot be distinguished by this method.) This method
is, of course, usable for ferroelectrics having no para-
electric phase transformation. Especially, in order to
distinguish the kinds in (a) from the kinds in (b), this
method is the most effective of the three. At present,
there are not many data on the comparison of the space
lattices in the two ferroelectric states.

In the following section we mainly use the first
method. This is due to the availability of data. But we
also take this occasion to see the characters—primitive-
ness or nonprimitiveness—of the paraelectric phase
transformations of actual ferroelectrics; this incidental
work will help in our future studies.

2. DETERMINATION OF THE KIND FOR ACTUAL FERROELECTRICS

We shall now discuss the determination of the kinds
of actual ferroelectrics. Since a group of ferroelectrics
that are isomorphous with one another should belong to

the same kind, we select only one example—a most typical one—from them. The order in which the ferroelectrics are discussed below is of little significance.

Triglycine sulfate[5] $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ belongs to space group $P2_1$ in the ferroelectric phase and to space group $P2_1/m$ in the paraelectric phase. According to Ref. 4, this phase transformation agrees with a primitive phase transformation of the ferroelectrics belonging to kind $r2$, and not with any primitive phase transformation of the ferrolectrics belonging to kind $i2$-I or $i2$-II. Therefore, it is concluded that ferroelectric triglycine sulfate belongs to kind $r2$, and incidentally, that this ferroelectric has a primitive phase transformation.

Diglycine nitrate[6] $(NH_2CH_2COOH)_2 \cdot HNO_3$ belongs to space group Pc in the ferroelectric phase and to space group $P2_1/c$ in the paraelectric phase. (The coordinate axes are set in the same way as in Ref. 4.) Therefore, it turns out that ferroelectric diglycine nitrate belongs to kind rm and has a primitive phase transformation.

Rochelle salt $NaKC_4H_4O_6 \cdot 4H_2O$ has two Curie temperatures. This is ferroelectric between these temperatures, and paraelectric both below the lower Curie temperature and above the upper Curie temperature. The ferroelectric phase belongs to point group 2, and both paraelectric phases belong to point group 222. Therefore, ferroelectric Rochelle salt is an irregular ferroelectric belonging to kind $i2$-II, and both of its two paraelectric phase transformations are primitive. The former conclusion can also be obtained from the observational fact that in ferroelectric Rochelle salt, the space lattice in one of the two stable states is such as is obtained by reflecting the space lattice in the other across a plane parallel to the diad axis of symmetry.

Sodium nitrite[7] $NaNO_2$ belongs to space group $Imm2$ in the ferroelectric phase, and to space group $Immm$ in the paraelectric phase. Recently, Hoshino et al. have proposed that an antiferroelectric phase should exist in a temperature range of about one degree between these ferroelectric and paraelectric phases. If this is true, the phase transformation $Imm2 \rightarrow Immm$ becomes indirect. To determine the kind of the ferroelectric phase, however, we should consider this virtual phase transformation. It is concluded that ferroelectric sodium nitrite belongs to kind $rmm2$.

In barium titanate $BaTiO_3$, four phases are known whose space groups are $Pm3m$, $P4mm$, $Amm2$, and $R3m$, respectively. The cubic phase is paraelectric, and the other three phases are ferroelectric. The tetragonal phase should belong to kind $r4mm$ since the point group

$4mm$ comprises this kind alone. Which kind, $rmm2$ or $imm2$, the orthorhombic phase should belong to can be determined by the third method mentioned in Sec. 1. In consequence, this phase must belong to kind $rmm2$. The rhombohedral phase must belong to kind $r3mR$ since any ferroelectric of space group $R3m$ must belong to this kind.[4]

The phase transformation from the tetragonal to the cubic phase of barium titanate is not primitive but complex, since point group $m3m$ is a supergroup of point group $4/mmm$. In single crystals of tetragonal barium titanate, therefore, domains more complicated than 180° are expected to be observed; in fact, the frequent emergence of 90° domains is well known. The phase transformations from the orthorhombic to the cubic phase and from the rhombohedral to the cubic phase do not actually occur. However, if their occurrence is assumed, they are complex, since point group $m3m$ is a supergroup of point groups mmm and $\bar{3}m$.

Lithium trihydrogen selenite[8] $LiH_3(SeO_3)_2$ is a ferroelectric belonging to point group m. This has no paraelectric phase transformation. Fortunately, there is an observation by Berlincourt et al. of the ferroelectric transformation of the piezoelectric-modulus tensor. According to it, since the nonzero elements of the tensor are all reversed in sign with the state transition, this ferroelectric must belong to kind rm.

Colemanite[9] $CaB_3O_4(OH)_3 \cdot H_2O$ belongs to point group 2 in the ferroelectric phase, and to point group $2/m$ in the paraelectric phase. Therefore this phase transformation is primitive, and this ferroelectric belongs to kind $r2$.

In potassium dihydrogen phosphate (often abbreviated KDP) KH_2PO_4, the phase transformation is $mm2 \rightarrow \bar{4}2m$, and hence primitive; the kind is $imm2$. This conclusion about the kind can also be obtained from the observational fact that in this ferroelectric the space lattice in one of the two stable states is such as is obtained by rotating the space lattice in the other by 90° about the diad axis of symmetry.

In ammonium sulfate[10] $(NH_4)_2SO_4$, the phase transformation is $Pna2_1 \rightarrow Pnam$ and hence primitive; the kind is $rmm2$.

In rubidium bisulfate[11] $RbHSO_4$, the phase transformation is $Pc \rightarrow P2_1/c$ and hence primitive; the kind is rm.

Methylammonium aluminum sulfate dodecahydrate[12] (often abbreviated MASD) $(NH_3CH_3)Al(SO_4)_2 \cdot 12H_2O$ belongs to point group 2 (space group $P2_1$) in the ferroelectric phase and to point group 23 (space group $P2_13$)

[5] B. T. Matthias, C. E. Miller, and J. P. Remeika, Phys. Rev. 104, 849 (1956); E. A. Wood and A. N. Holden, Acta Cryst. 10, 145 (1957); R. Pepinsky, Y. Okaya, and F. Jona, Bull. Am. Phys. Soc. 2, 220 (1957).

[6] R. Pepinsky, K. Vedam, S. Hoshino, and Y. Okaya, Phys. Rev. 111, 430 (1958).

[7] S. Sawada, S. Nomura, S. Fujii, and I. Yoshida, Phys. Rev. Letters 1, 320 (1958); Y. Yamada, I. Shibuya, and S. Hoshino, J. Phys. Soc. Japan 18, 1594 (1963); S. Hoshino, J. Phys. Soc. Japan 19, 140 (1964).

[8] R. Pepinsky and K. Vedam, Phys. Rev. 114, 1217 (1959); D. Berlincourt, W. R. Cook, Jr., and M. E. Rander, Acta Cryst. 16, 163 (1963).

[9] C. L. Christ, Am. Mineralogist 38, 411 (1953); G. J. Goldsmith, Bull. Am. Phys. Soc. 1, 322 (1956); F. Holuj and H. E. Petch, Can. J. Phys. 36, 145 (1958).

[10] B. T. Matthias and J. P. Remeika, Phys. Rev. 103, 262 (1956).

[11] R. Pepinsky and K. Vedam, Phys. Rev. 117, 1502 (1960).

[12] R. Pepinsky, F. Jona, and G. Shirane, Phys. Rev. 102, 1181 (1956).

in the paraelectric phase. Point group 23 is a supergroup of point group 222, but not of point group $2/m$ nor of point group $\bar{4}$. Therefore, this phase transformation must be complex, and this ferroelectric must belong to kind $i2$-II. In single crystals of this ferroelectric, the emergence of 90° domains is anticipated. (It seems that this is not yet confirmed.)

Thiourea[13] $(NH_2)_2CS$ is ferroelectric at temperatures below 169°K, and paraelectric at temperatures above 202°K. Between 169 and 202°K, it appears that three or four transient phases occur; their natures are, at present, not very clear, although it has been proposed by Goldsmith and White that one of them is ferroelectric and others antiferroelectric. In order to determine the kind of the principal ferroelectric phase (existing below 169°K), however, we need not consider these transient phases, as in the case of $NaNO_2$. The principal ferroelectric phase belongs to space group $Pmc2_1$, and the principal paraelectric phase (existing above 202°K) belongs to space group $Pmcn$. Therefore, it is considered that the phase transformation between these phases, though indirect, is primitive, and that this ferroelectric belongs to kind $rmm2$.

For ammonium monochloroacetate[14] $ClCH_2COONH_4$, the phase transformation is $m \rightarrow 2/m$, and hence primitive; the kind is rm.

In dicalcium strontium propionate[15] $Ca_2Sr(C_2H_5COO)_6$, the phase transformation is $4 \rightarrow 422$. Therefore, it is considered that this ferroelectric belongs to either the kind $r4$-II or $i4$, and that this phase transformation is primitive. At present, since there are not more data, we cannot determine which kind, $r4$-II or $i4$, this ferroelectric belongs to. (For this determination, the second and third methods—especially the third method—mentioned in Sec. 1 may be suitable.)

In potassium ferrocyanide trihydrate[16] $K_4Fe(CN)_6 \cdot 3H_2O$, the phase transformation is $m \rightarrow 2/m$ and hence primitive; the kind is rm.

Guanidinium aluminum sulfate hexahydrate[17] (often abbreviated GASH) $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$ is a ferroelectric belonging to space group $P31m$ and has no paraelectric phase transformation. In general, a ferroelectric of space group $P31m$ must belong[4] to either the kind $r3mP$-I or $r3mP$-II. At present there are not sufficient data to determine conclusively which of these kinds GASH should belong to. From the crystal structure proposed by Geller and Booth, however, it is presumed that the state transition of GASH is of inversion type rather than of reflection type, and hence, that its kind is $r3mP$-I rather than $r3mP$-II. (For the final determination, the first and third methods are of no service; the observation of the ferroelectric transformation of a suitable tensorial property is desired.)

Lithium niobate[18] $LiNbO_3$ is a ferroelectric belonging to space group $R3c$ and has no paraelectric phase transformation. Since any ferroelectric of space group $R3c$ must belong[4] to kind $r3mR$, lithium niobate must belong to this kind. (If a crystal belonging to a polar group exhibits a dielectric hysteresis loop and has a phase transformation that appears to be primitive or complex, this crystal will almost certainly be ferroelectric. If it only exhibits a dielectric hysteresis loop and does not have a phase transformation, other facts are necessary for determining its ferroelectricity. Lithium niobate is one such case. Although this crystal is very probably ferroelectric, more proof is yet needed.)

In potassium nitrate[19] KNO_3, three phases I, II, and III are known whose space groups are $R\bar{3}m$, $Pmnb$, and $R3m$, respectively. Phase III is ferroelectric and the other two phases are paraelectric. At room temperature, phase II is the most stable, and at high temperatures phase I is the most stable; phase III occurs only as a metastable state. It is reported that on lowering the temperature, phase I transforms first to phase III and then to phase II; on raising the temperature, phase II transforms directly to phase I, not via phase III. Since any ferroelectric of space group $R3m$ must belong to kind $r3mR$, ferroelectric potassium nitrate must belong to this kind. The phase transformation from III to I is primitive, but the phase transformation from III to II is neither primitive nor complex, since the point group mmm of phase II is not a supergroup of point group $3m$. In general, it is anticipated that paraelectric phase transformations of the ferroelectrics existing only as a thermodynamically metastable state may often be nonprimitive and noncomplex.

For antimony sulfoiodide[20] $SbSI$, the phase transformation is $Pna2_1 \rightarrow Pnam$ and hence primitive; the kind is $rmm2$.

Tetramethylammonium mercury tribromide[21] $N(CH_3)_4HgBr_3$ is a ferroelectric belonging to space group $P2_1$ and has no paraelectric phase transformation.

[13] R. W. G. Wyckoff and R. D. Corey, Z. Krist. 81, 386 (1932); A. L. Solomon, Phys. Rev. 104, 1191 (1956); G. J. Goldsmith and J. G. White, J. Chem. Phys. 31, 1175 (1959); H. Futama, J. Phys. Soc. Japan 17, 434 (1962).

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[15] B. T. Matthias and J. P. Remeika, Phys. Rev. 107, 1727 (1957); P. Orioli and M. Pieroni, Ricerca Sci. 29, 295 (1959).

[16] S. Waku, H. Hirabayashi, H. Toyoda, H. Iwasaki, and R. Kiriyama, J. Phys. Soc. Japan 14, 973 (1959); S. Waku, K. Masuno, T. Tanaka, and H. Iwasaki, ibid. 15, 1185 (1960).

[17] A. N. Holden, B. T. Matthias, W. J. Merz, and J. P. Remeika, Phys. Rev. 98, 546 (1955); E. A. Wood, Acta Cryst. 9, 618 (1956); S. Geller and D. P. Booth, Z. Krist. 111, 117 (1959).

[18] B. T. Matthias and J. P. Remeika, Phys. Rev. 76, 1886 (1949); P. Bailey, thesis, Bristol, 1952 (unpublished); H. D. Megaw, Acta Cryst. 7, 187 (1952); Y. Shiozaki and T. Mitsui, Phys. Chem. Solids 24, 1057 (1963).

[19] S. Sawada, S. Nomura, and S. Fujii, J. Phys. Soc. Japan 13, 1549 (1958).

[20] E. Dönges, Z. Anorg. Allgem. Chem. 265, 56 (1951); E. Fatuzzo, G. Harbeke, W. J. Merz, R. Nitsche, H. Roetschi, and W. Ruppel, Phys. Rev. 127, 2036 (1962); K. Toyoda and I. Shibuya, notes for the 1963 autumn meeting of the Phys. Soc. Japan, p. 330 (unpublished).

[21] E. Fatuzzo and R. Nitsche, Phys. Rev. 117, 936 (1960); E. Fatuzzo, R. Nitsche, H. Roetschi, and S. Zingg, ibid. 125, 514 (1962); J. G. White, Acta Cryst. 16, 397 (1963).

At present there are not sufficient data to determine conclusively which of three kinds $r2$, $i2$-I, and $i2$-II this ferroelectric should belong to. From the crystal structure proposed by White, however, it is presumed that the state transition type of this ferroelectric is reflection rather than rotation or rotatory reflection, and hence, that its kind is most probably $r2$.

Ammonium cadmium sulfate[22] $(NH_4)_2Cd_2(SO_4)_3$ is reported to be paraelectric above a temperature of about 90°K and to exhibit a dielectric hysteresis loop below this temperature. The high-temperature phase belongs to point group 23 (space group $P2_13$). The point group of the low-temperature phase, however, is unknown. Let us assume the low-temperature phase to be ferroelectric, as Jona and Pepinsky asserted, and infer its kind from only the above-mentioned information on the point group of the paraelectric phase. (The low-temperature phase is very probably ferroelectric. For a conclusive determination, however, more proofs are desired. For instance, if its point group becomes known and, moreover, as being such that the phase transformation appears to be primitive or complex, it is almost certainly ferroelectric.) Since, by a primitive phase transformation, no kind transforms to the paraelectric point group 23, the phase transformation of ammonium cadmium sulfate must be nonprimitive. Let us assume it to be complex, since a nonprimitive and noncomplex phase transformation is expected to be exceptional. The kind of ferroelectric ammonium cadmium sulfate, then, must be one of those kinds which transform to a subgroup of point group 23 by a primitive phase transformation. We enumerate all the subgroups of point group 23:

$$1, \quad 2, \quad 222, \quad 3.$$

There is no kind which transforms to point group 1 or 3 by a primitive phase transformation. For point group 2, there is kind $i1$-II, and only this. For point group 222, there is kind $i2$-II, and only this. In consequence, the kind of ferroelectric ammonium cadmium sulfate must be either $i1$-II or $i2$-II. At present, we cannot go further than this stage.

We have now finished determining the kinds of actual ferroelectrics and, incidentally, examining the characters of their paraelectric phase transformations. The results are tabulated. Table I does not include all of the representatives of the ferroelectrics discovered until now, but we think most are there; we have excluded those which are not established as ferroelectrics, and those for which there are not enough reliable data. From Table I we see the following.

Every actual ferroelectric does belong to one of the 30 kinds, as has been expected. On the other hand, not all of the 30 kinds have actual ferroelectrics belonging to them; "empty" kinds, however, might in future be occupied.

Of the actual ferroelectrics having a paraelectric phase

[22] F. Jona and R. Pepinsky, Phys. Rev. **103**, 1126 (1956).

TABLE I. The kinds of actual ferroelectrics and the characters of their paraelectric phase transformations.

Ferroelectric crystal	Kind	Paraelectric phase transf.
Triglycine sulfate	$r2$	Primitive
Diglycine nitrate	rm	Primitive
Rochelle salt	$i2$-II	Primitive
$NaNO_2$	$rmm2$	Primitive
Tetragonal $BaTiO_3$	$r4mm$	Complex
Orthorhombic $BaTiO_3$	$rmm2$	None
Rhombohedral $BaTiO_3$	$r3mR$	None
$LiH_3(SeO_3)_2$	rm	None
Colemanite	$r2$	Primitive
KH_2PO_4	$imm2$	Primitive
$(NH_4)_2SO_4$	$rmm2$	Primitive
$RbHSO_4$	rm	Primitive
MASD	$i2$-II	Complex
Thiourea	$rmm2$	Primitive
$ClCH_2COONH_4$	rm	Primitive
$Ca_2Sr(C_2H_5COO)_6$	$r4$-II or $i4$	Primitive
$K_4Fe(CN)_6 \cdot 3H_2O$	rm	Primitive
GASH	$r3mP$-I (?)	None
$LiNbO_3$	$r3mR$	None
KNO_3	$r3mR$	Primitive
SbSI	$rmm2$	Primitive
$N(CH_3)_4HgBr_3$	$r2$ (?)	None

transformation, only barium titanate and MASD—and their isomorphs—have a complex phase transformation; all the others have a primitive one. (If the low-temperature phase of ammonium cadmium sulfate is indeed ferroelectric, its paraelectric phase transformation is probably complex.) The irregular ferroelectrics are only Rochelle salt, potassium dihydrogen phosphate, and MASD (and dicalcium strontium propionate?); all the others are regular. (If ammonium cadmium sulfate becomes ferroelectric, it is probably irregular.)

We remark especially upon the kinds $i1$-I, $i1$-II, and im. It seems that no ferroelectrics belonging to these kinds have yet been discovered. If a ferroelectric belonging to one of these kinds exists and makes a primitive phase transformation, its paraelectric phase should[4] belong to the *polar* point group m, 2, or $mm2$ (according to whether the kind of the ferroelectric is $i1$-I, $i1$-II, or im). One might expect this paraelectric phase to exhibit ferroelectricity because of its belonging to a polar group, and apply an electric field in a direction parallel to the mirror plane of symmetry (for the point group m) or in the direction of the diad axis of symmetry (for the point group 2 or $mm2$). Then one would find, however, that no polarization reversal occurs. This phase is "hard" in this direction. It is rather "soft" in the direction perpendicular to the mirror plane of symmetry (for the point group m) or in a certain direction perpendicular to the diad axis of symmetry (for the point group 2) or in the direction perpendicular to one of the two mirror planes of symmetry (for the point group $mm2$). If one undertook to observe dielectric susceptibilities, one would find that the Curie-Weiss law holds most conspicuously in this direction. (The author has made this remark to suggest a way of discovering ferroelectrics of the kinds $i1$-I, $i1$-II, and im.)

KÊITSIRO AIZU

Finally, we note that the present results serve for finding *gyroelectrics* and *hypergyroelectrics* among known ferroelectrics. The gyroelectrics and the hypergyroelectrics are[23,3] those crystals whose gyration (or optical rotatory power) and *electrogyration*, respectively, are nonzero at zero electric field and reversible in sign by means of an electric field; here electrogyration is defined[23,3] as the rate of change of the gyration with the electric field at zero value of the electric field. The gyroelectric and hypergyroelectric crystals must be

ferroelectric. Which of the actual ferroelectrics should be gyroelectric, which hypergyroelectric, and which neither gyroelectric nor hypergyroelectric can readily be found by comparing Table I in the present paper with Tables IV and V in Ref. 3. (Since SbSI is not very transparent, it is unsuitable for use as a gyroelectric.)

ACKNOWLEDGMENT

[23] K. Aizu, Phys. Rev. **133**, A1584 (1964).

Far-Infrared Electronic Transitions in Ions and Pairs of Ions

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In ruby (1% Cr_2O_3), we found two dichroic lines at 100 and 270 μ; in pure praseodymium chloride, two dichroic lines at 100 and 325 μ; in diluted samarium chloride (5%Sa^{3+} in $LaCl_3$), two lines at 100 and 250 μ. A tentative explanation is given for all these lines as transitions between sublevels of the ground-state split either by the crystalline field or by exchange forces between neighboring ions.

I. INTRODUCTION

FOR a few years, we have known that all crystals become as completely transparent in the far infrared at liquid-helium temperature[1] as they generally are in the visible at room temperature. So it is possible to search for electronic transitions of ions imbedded in various lattices. Of course they are low-frequency transitions. The very close levels which take part may be the different components of the ground level of an ion slightly split by the crystal field (as the case with the $4f$ states of rare-earth ions, where the $4f$ electrons are generally considered as well shielded from the crystal field). However, there are other splitting possibilities, for instance slight coupling between two neighbor ions. This paper will show that both types of transitions lead to absorption lines whose intensity is far from negligible.
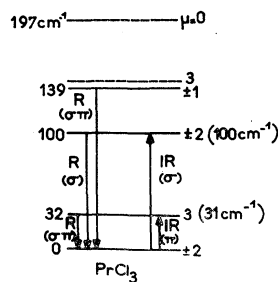

FIG. 1. Stark splitting of the $^3H_4$ ground state of Pr^{3+} in pure $PrCl_3$.

[1] A. Hadni, J. Claudel, E. Decamps, X. Gerbaux, and P. Strimer, Compt. Rend. **255**, 1595 (1962).

II. RARE-EARTH IONS

1. Anhydrous Praseodymium Chloride

The praseodymium ion has two $4f$ electrons and the total angular momentum is $J=4$. (In a magnetic field, each J state is split into $2J+1$ sublevels characterized by the quantum number M_J.) In pure praseodymium chloride, each Pr^{3+} ion is in an electric field of C_{3h} symmetry and the 9 components will include 3 Kramers doublets. Their symmetry is given either by the classical notation $A'A''E''E'$ or the Hellwege's quantum crystal numbers $\mu=0, 3, \pm1, \pm2$, respectively. The selection rules for electric-dipole transitions are

	A' $\mu=0$	E'' $\mu=\pm1$	E' $\mu=\pm2$	A'' $\mu=3$
A' $(\mu=0)$	$\cdots$	$\cdots$	σ	π
E'' $(\mu=\pm1)$	$\cdots$	σ	π	σ
E' $(\mu=\pm2)$	σ	π	σ	$\cdots$
A'' $(\mu=3)$	π	σ	$\cdots$	$\cdots$.

All but two sublevels (in dotted lines), are given on Fig. 1 by the spectroscopy, in the visible, of doped lanthanum chloride single crystals at liquid-helium temperature. All these levels, and another one at 197 cm^{-1} [tentatively interpreted as the A' $(\mu=0)$ missing one], have given electronic Raman lines in a sample of pure praseodymium chloride.[2]

[2] J. T. Hougen and S. Singh, Phys. Rev. Letters **10**, 406 (1963).