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PARAELECTRIC REFRIGERATION METHOD AND APPARATUS

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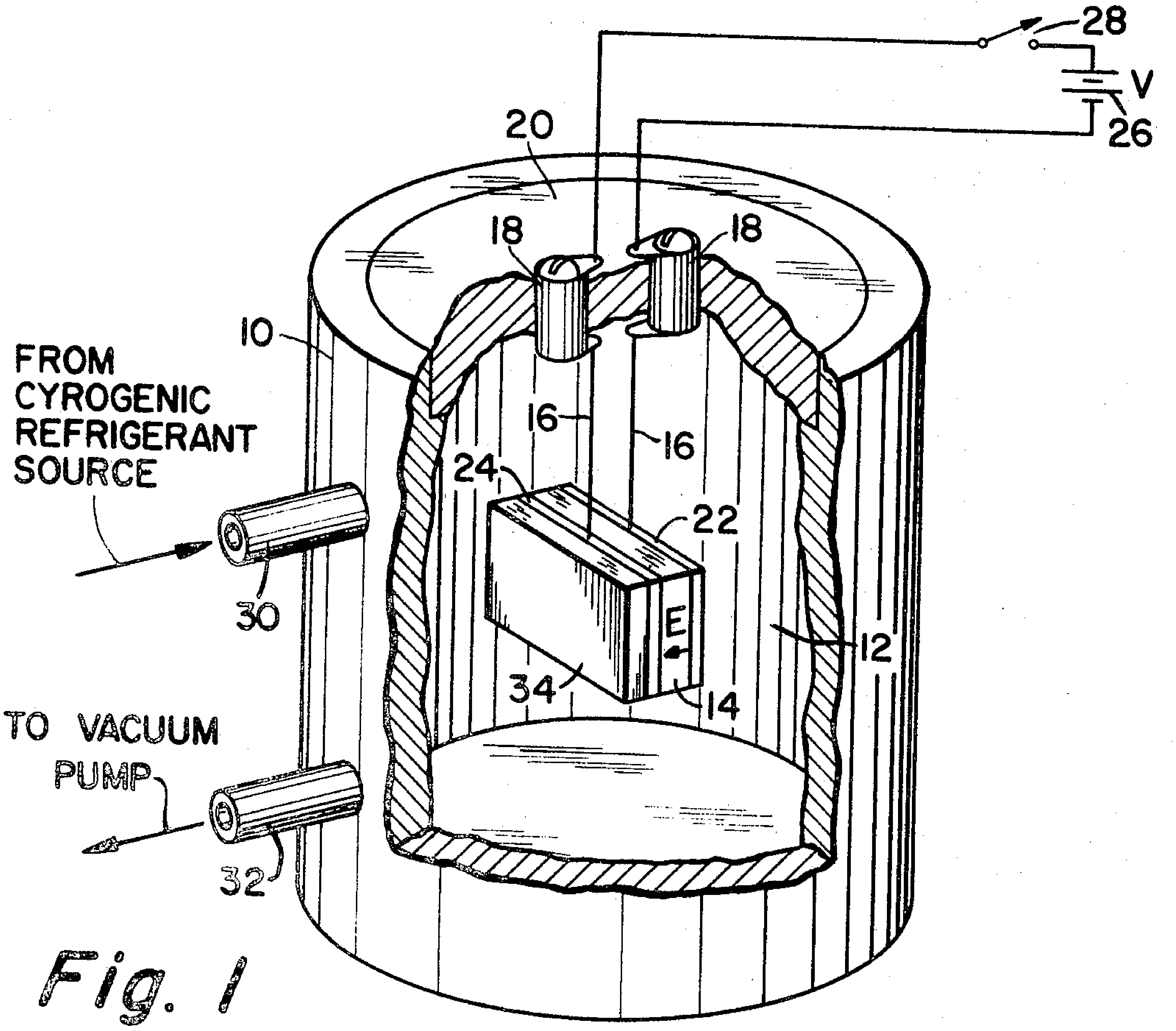

Fig. 1

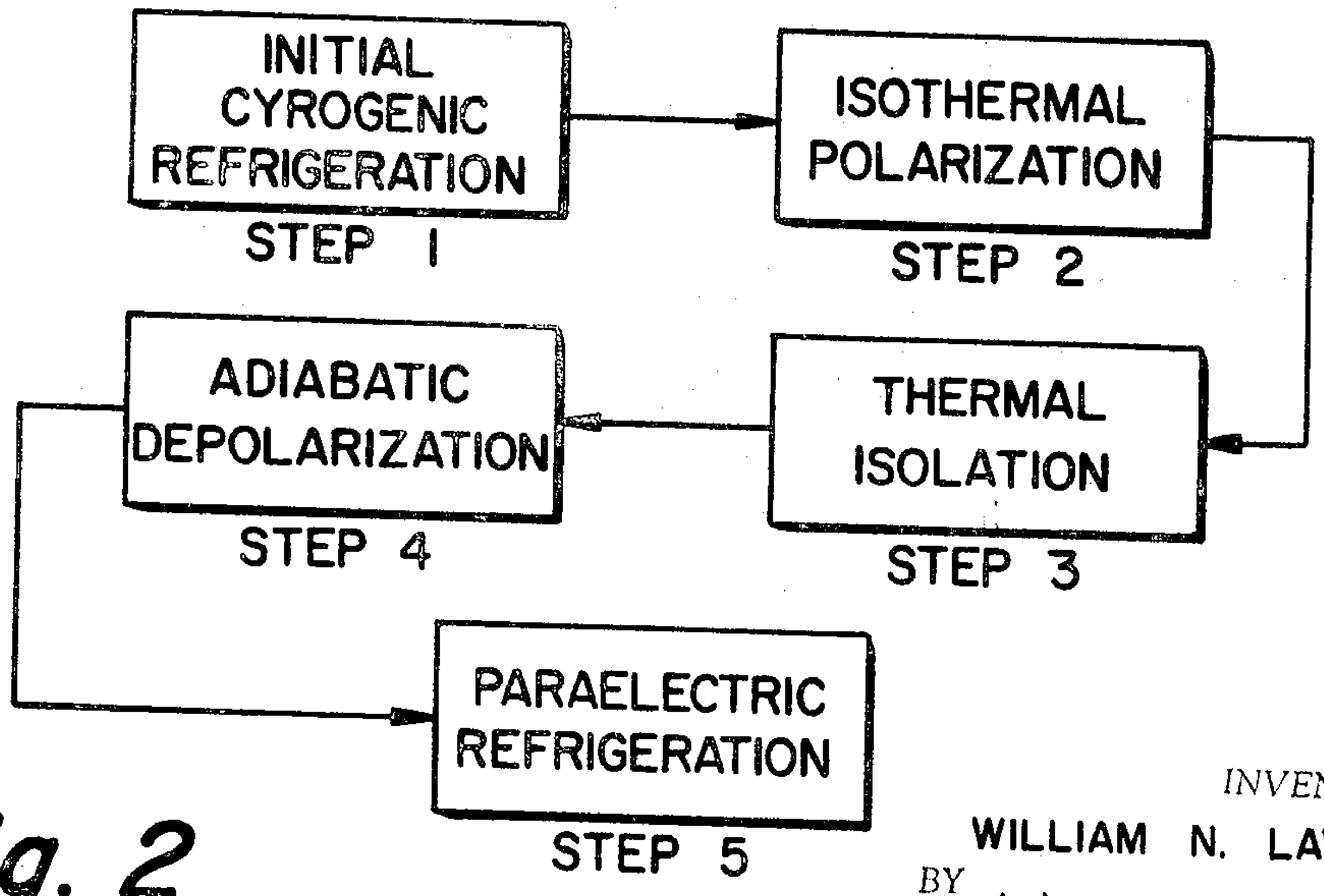

Fig. 2

INVENTOR.
WILLIAM N. LAWLESS
BY Walter S. Zaborski
ATTORNEY

United States Patent Office

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PARAELECTRIC REFRIGERATION METHOD AND APPARATUS

William N. Lawless, Corning, N.Y., assignor to Corning Glass Works, Corning, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

A refrigerator and cooling method employing a paraelectric refrigerant consisting of a material having a rutile-like crystalline lattice structure doped with polar impurity ions. The refrigerant is cooled by conventional hydrogen or helium cryogenic cooling means to a temperature within its paraelectric refrigeration range. An electric field is applied to the refrigerant to produce isothermal polarization of the hydroxyl ion electric dipoles thereby decreasing the entropy of the refrigerant. Thereafter the refrigerant is thermally isolated, and the electric field is removed causing the impurity ion electric dipoles to adiabatically depolarize resulting in paraelectric cooling of the refrigerant.

Background of the invention

The development in recent years of devices and systems which function under cryogenic conditions, such as cryogenic computer memories, high efficiency gallium arsenide diodes, high-field superconducting alloys, masers, and the like has lead to a search for more economical and less complex means for obtaining cryogenic environments. To achieve temperatures on the order of 1° K., highly complex and expensive cryogenic pumping systems using helium as a refrigerant have been required.

In some cases several types of helium cooling systems have been combined to achieve extremely low temperatures. For example, the conventional helium cryostat cooling system has been used to produce temperatures on the order of 4° K., at which point the well-known helium pump has been employed to produce additional cooling to temperatures as low as about 1° K. Another helium operated apparatus, commonly known in the art as an Oxford instrument, has also been used in combination with the helium pump system to provide cryogenic environments as low as 0.05° K.

Elaborate helium cooling systems have also been used to cool paramagnetic refrigerant materials to intermediate temperatures sufficient to initiate paramagnetic cooling processes. Though temperatures as low as about 0.001° K. have been achieved by paramagnetic cooling methods, the maximum starting temperature from which effective paramagnetic cooling can be initiated is only about 1.2° K. Such low starting temperatures are not obtainable by means other than the most complex helium refrigeration systems.

More recently paraelectric refrigeration effects produced by the adiabatic depolarization of hydrozyl doped potassium chloride refrigerants, KCl:OH, have been demonstrated. Because they can be initiated at considerably higher starting temperatures than can paramagnetic processes, paralelectric processes provide a much simpler and more economical means of achieving low temperatures. Paraelectric cooling processes are obtainable starting at temperatures as high as about 20° K., although higher temperatures may be usable. These starting temperatures are easily within the reach of simple helium cryogenic cooling apparatus such as the conventional helium cryojet. Moreover relatively simple cryogenic

cooling systems using inexpensive hydrogen refrigerants are also capable of providing paraelectric starting temperatures.

However, a difficulty encountered in heretofore known paraelectric cooling methods has been their inability to achieve extremely low temperatures in comparison to those achieved by paramagnetic methods. Experimentation with KCl:OH paraelectric refrigerants has produced minimum temperatures of only about 0.3° K. These minimum temperatures have been found to be, in part, dependent upon the concentration of impurity ions in the host crystalline materials, the starting temperature at which paraelectric cooling is initiated, the particular composition and structural characteristics of the host crystalline material, and the intensity of the polarizing electric field employed in the process.

I have found that the minimum temperatures attainable paraelectrically using heretofore known paraelectric refrigerants are limited by the antiparallel correlation or alignment of interacting impurity ion electric dipoles. To illustrate the deleterious effect such interactions have on paraelectric cooling processes known in the art consider the ordinary paraelectric refrigerant, hydroxyl doped KCl.

In order to initiate paraelectric refrigeration the material is initially cooled by conventional cryogenic means to an intermediate temperature. This temperature, being the paraelectric starting temperature, is sufficiently low to permit isothermal polarization of the impurity ion electric dipoles through the application to the refrigerant of a biasing electric field. Such polarization lowers the potential energy of the impurity dipole system rapidly, to the extent that the dipoles are aligned, and produces a substantial decrease in the entropy of the refrigerant. The heat of polarization generated thereby is absorbed by the cooling reservoir of the cryogenic refrigerator so as to cause polarization to occur in a substantially isothermal manner.

While maintaining polarization with the electric field the refrigerant is thermally isolated from all external thermal influences while at the paraelectric starting temperature. Thereafter paraelectric cooling is initiated by removing the electric field thus permitting the impurity dipoles to depolarize adiabatically. With the polarizing influence of the electric field removed a portion of the phonon spectrum thermal energy contained in the host crystal lattice produces randomization of previously aligned electric dipole moments and, in so doing, is converted into potential energy in the dipole system. Since depolarization occurs adiabatically energy is conserved within the refrigerant and paraelectric refrigeration continues so long as dipole randomization continues.

However, in the KCl:OH refrigerant, interactions between neighboring pairs of impurity dipoles occur as the refrigerant's temperature decreases. These interactions produce anti-parallel alignment of dipole pairs resulting in the vectoral cancellation of their net dipole moments. With no net dipole moment an anti-parallel aligned pair is not available to reduce thermal lattice energy through further randomization of the pair members. Consequently, such a dipole pair cannot aid in the further reduction of the refrigerant's temperature.

The effects of such interactions are illustrated by noting the behavior of the refrigerants dielectric constant as the temperature decreases through the paraelectric cooling range. As is well known to those skilled in the art, the dielectric constant of a paraelectric material is temperature dependent over its paraelectric cooling range, exponentially increasing as the temperature decreases to a point, and thereafter leveling off to a maximum value. The temperature corresponding to the maximum dielectric constant is the equilibrium temperature of the material and is the lowest temperature attainable paraelectrically using a given refrigerant. Though some adjustment can be made in the equilibrium temperature value by adjusting the impurity concentration, minimum values of about 0.3° K. are the lowest that have heretofore been achieved. In any case, the lowest temperatures that have been achieved paraelectrically are limited as a result of anti-parallel dipole pair alignments. The refrigerant reaches its equilibrium temperature when pair alignment of the dipoles become complete such that no further randomization can take place. Accordingly, no further reduction in thermal energy is possible and the refrigerant ceases to cool.

I have found that certain heretofore unknown paraelectric materials exist whose impurity ion electric dipoles interact at low temperatures, but in such manner as to produce parallel alignment or correlation of neighboring impurity dipole pairs. These materials do not have the severe minimum temperature restrictions of the heretofore known paraelectric refrigerants because their impurity ion electric dipole moments do not cancel pairwise at low temperatures. A net dipole moment exists in parallel aligned dipole pairs rendering such pairs available for randomization under the influence of lattice thermal energy.

Moreover I have found that parallel dipole pair alignments actually enhance paraelectric refrigerant capabilities. Such interactions produce a greater rate of increase in the dielectric constant with temperature decrease than in the case with the heretofore known refrigerants. Such an increase in the dielectric constant can be expected to continue until low temperatures are reached at which quantum effects become appreciable. Further, while lower minimum temperatures are obtainable paraelectrically with these new materials than has heretofore been possible using KCl:OH refrigerants, the advantages of comparatively high paraelectric starting temperatures are retained.

Summary of the invention

It is therefore an object of the instant invention to provide a paraelectric refrigerator having the ability to cool materials to lower temperatures than heretofore possible.

It is a further object of the instant invention to provide a more economical method for achieving low temperatures than has heretofore been possible.

Briefly, in accordance with the instant invention, a paraelectric refrigerant, having a rutile-like crystalline lattice structures containing polarizable impurity ions which occupy the bond of the structure which corresponds to the 2.52 A. oxygen-oxygen bond of rutile and whose electric dipole moments are alignable in the *a—a* crystal plane, is cooled to a temperature within its paraelectric refrigeration range. Thereafter an electric field is applied to the refrigerant in such manner as to cause isothermal polarization of the impurity ions thereby aligning at least a portion of their electric dipole moments and reducing the entropy of the refrigerant. Thereafter the refrigerant is thermally isolated. Thereafter the electric field is removed such that the refrigerant cools paraelectrically by adiabatic depolarization of the impurity ions.

Additional objects, features, and advantages of the instant invention will become apparent to those skilled in the art from the following detailed description and attached drawings, on which, by way of example, only the preferred embodiment of the instant invention are illustrated.

Brief description of the drawing

FIG. 1 shows an oblique cutaway view of a paraelectric refrigerator illustrating one embodiment of the instant invention.

FIG. 2 illustrates the steps in the method of the instant invention.

Description of the preferred embodiments

By paraelectric is meant that property of a material which enables its dielectric constant ϵ to follow the mathematical relation

$$\epsilon \propto (T-T_0)^{-1}, \text{ for } T>T_0$$

within some temperature range. The term T_0 is the Curie point of the material and the term T is its temperature.

By paraelectric refrigeration range is meant that range of temperatures through which the dielectric constant of the material varies in accordance with the above stated mathematical relationship.

The terms polarization and depolarization as used herein relate to the orientation of the electric dipole moments of polar impurity ions in paraelectric materials.

By rutile-like crystalline lattice structure is meant crystalline structures of the various materials whose geometric patterns are characterized by that of rutile.

Referring to FIG. 1 there is provided a cryogenic refrigerator **10** of a type well known in the art such as cryojet, cryostat, helium pump, or the like. Such a refrigerator **10** utilizes conventional hydrogen or helium refrigerants and for purposes of the instant invention must have the capacity to cool a material within its refrigeration chamber or reservoir **12** to a temperature at which the paraelectric properties of the material can be effectively utilized. Ordinarily this temperature is as high as about 20° K. although some degree of paraelectric behavior is present in these materials at higher temperatures.

A paraelectric refrigerant **14** is provided being selected from the group of materials having rutile-like crystalline lattice structures such as TiO_2, SnO_2, PbO_2, and the like and being appropriately doped with a polar ion impurity. Any polar ion capable of occupying the 2.52 A. oxygen-oxygen bond of the rutile-like lattice structure and having an electric dipole moment alignable in the *a—a* crystal plane, such as the hydroxyl ion, is a suitable impurity for purposes of the instant invention. The polar impurity ion concentration required in order to permit the refrigerant **14** to cool paraelectrically is not critical and may range in value from about 10^{18} cm.$^{-3}$ up to about 10^{21} cm.$^{-3}$. Ordinarily an impurity concentration on the order of about 10^{18} cm.$^{-3}$ is satisfactory and will permit the refrigerant **14** to cool paraelectrically from a starting temperature as high as about 20° K. The exact impurity concentration required to produce optimum cooling depends upon the temperature at which paraelectric cooling is to be started. In any case this temperature must be within the refrigerants paraelectric range wherein the dielectric constant is substantially temperature dependent and this range of temperatures is a function of impurity concentration.

The impurity ions may be implanted in the rutile-like crystalline material by any suitable means well known in the art. For example, rutile may be doped with hydroxyl impurities by passing hydrogen gas through rutile particles at high temperatures. Thereafter the particles are sinter pressed into the desired physical shape thereby providing a TiO_2:OH paraelectric refrigerant. It is desirable to provide the refrigerant **14** in the shape of a thin sheet or disc in order to permit a high electric potential gradient to occur through the material upon application of an electric field as later explained.

The refrigerant **14** is suspended within the chamber **12** by means of two electrically conducting wires **16** so as to avoid physical contact with the chamber defining surfaces. This provides the ability to thermally isolate the refrigerant **14** while maintaining the refrigerant **14** in a polarized state. The conducting wires **16** are fixedly attached to the bottom terminals of suitable electrical feedthrough insulators **18** mounted in a refrigerator lid **20** so as to permit stable suspension of the refrigerant **14** within the chamber **12** and to provide means for electrically contacting the faces of the refrigerant **14** from without. The wires **16** should be as long, and as fine in diameter, as possible, in order to minimize heat conduction. Suspension of the refrigerant **14** by the conductive wires

16 may be accomplished by any suitable means well known in the art. One such method includes the application of an electroding paste **22** and **24** to the faces of the refrigerant **14** consisting essentially of an organic glue epoxy compound containing uniformly distributed particles of electroconductive material such as silver, gold, platinum, alloys thereof, or the like, in suspension. An end portion of one of the conductive wires **16** is embedded in the electrode paste layer **22** while the end portion of the remaining conductive wire **16** is embedded in the other electrode paste layer **24**. The assembly so formed is fired or baked at a temperature sufficient to solidify the paste **22** and **24**, and bind the paste **22** and **24** to the faces of the refrigerant **14** and to the end portions of the conductive wires **16**.

A direct current potential source **26** is connected across the refrigerant **14** by connecting it across the top terminals of the feed-through insulators **18**. The electrical potential supplied by the source **26** may be of any value sufficient to produce a polarizing electric field in the refrigerant **14**, the presence of which is illustrated by an arrow labeled E. It is desirable that the electric potential gradient be as large as possible in order to obtain the greatest alignment of impurity dipole moments. However, it must not be so large as to produce dielectric breakdown of the refrigerant **14**, or the surrounding atmosphere. The electric potential gradient across the material can be increased by increasing either the voltage supplied by the source **26** or by making the thickness of the refrigerant **14** smaller so as to bring the electrode layers **22** and **24** closer together or both. The magnitude of the electric field required to polarize the impurity dipoles depends upon the starting temperature of the refrigerant. Further, since the dielectric constant of the refrigerant **14** is somewhat higher at the starting temperature than is the case at room temperatures, the dielectric breakdown potential of the refrigerant **14** is likewise higher. An electric field on the order of 500,000 volts per centimeter is sufficient at a starting temperature not in excess of 20° K. However, in general, the lower the starting temperature, the lower the potential gradient required to produce a given quantity of polar alignments. A switch **28** series connected between the source **26** and the refrigerant **14** provides means for the application and removal of the electric field as necessary.

An inlet pipe **30** permits the introduction of a hydrogen or helium cryogenic refrigerant into the chamber **12** from an external source in order to cool the paraelectric refrigerant **14**, and such other materials as may be present therein, to the desired starting temperature. An exhaust pipe **32** is connected to a vacuum pump, not shown, as indicated in FIG. 1 by an arrow so as to permit removal of the hydrogen or helium atmosphere from the chamber **12**, and provide an effective vacuum whereby the refrigerant **14** and materials in thermal contact therewith, if any, is thermally isolated. As is well known to those skilled in the art, the lower the vacuum obtainable in the chamber **12**, the better will be the thermal isolation of the refrigerant **14** as a result. Chamber vacuums on the order of 10^{-6} mm. of mercury or less provide satisfactory thermal isolation for materials suspended therein for purposes of the instant invention.

Referring to FIGS. 1 and 2 the following is one example of the method of the instant invention and how it may be practiced. In order to cool a material **34** by the method of the instant invention the material **34** is placed in thermal contact with a paraelectric refrigerant **14** consisting of rutile doped with hydroxyl impurities to an impurity concentration of 10^{18} cm.$^{-3}$. In this manner the material **34** and the refrigerant **14** can be thermally isolated together at the same temperature in a following step as later explained. The material **34** to the paraelectric refrigerant **14** are secured to each other by means of the organic electrode paste layer **24**. This procedure is similar to that used to embed an end portion of one conductive wire **16** in the layer **24** as previously explained.

The assembly consisting of the electrode layers **22** and **24**, the paraelectric refrigerant **14**, and the material **34** to be cooled is suspended within the chamber **12** by means of the conductive wires **16**. In accordance with step **1** of FIG. 2 a helium cryogenic refrigerant is pumped into the chamber **12** thereby lowering the temperature of the refrigerant **14** and material **34** to a desired starting temperature T_1 within the paraelectric range of refrigerant **14**. A starting temperature of 20° K. or less is preferred though higher temperatures permit at least a small amount of paraelectric cooling.

Thereafter in accordance with step **2**, the paraelectric refrigerant **14** is subjected to an electric field of about 500,000 volts per centimeter by closing the switch **28**. This step is accomplished isothermally by permitting the helium atmosphere in the reservoir of the refrigerator **10** to absorb the heat of polarization being generated. Isothermal polarization of the impurity dipole moments produces a decrease in the entropy of the refrigerant **14**, and lowers the potential energy of the impurity dipole system to the extent that their electric dipole moments align.

Thereafter, in accordance with step **3**, the polarized refrigerant **14** and the material **34**, both at temperature T_1, are together thermally isolated from all external thermal influences by reducing the atmosphere within the chamber **12** to about 10^{-6} mm. of mercury or less with a vacuum pump.

In accordance with step **4** the switch **28** is opened removing the electric field from the refrigerant **14** thus depolarizing the hydroxyl impurities adiabatically. Step **4** is performed with negligible heat gain by the refrigerant **14** by providing the refrigerator **10** with suitable insulation in any manner well known in the art and by making the conductive wires **16** as long and as small in diameter as possible. Adiabatic depolarization of the hydroxyl impurities produces a rapid decrease in the temperature of the refrigerant **14** to a value T_2 as phonon spectrum thermal energy contained in the crystal lattice is reduced by conversion of a portion thereof to potential energy through randomization of the impurity ion electric dipole moments. The extent to which the refrigerant **14** cools as a result of step **4** depends upon the particular rutile-like crystalline material used in the refrigerant **14**, the impurity ion concentration therein, the magnitude of the polarizing electric field, and the paraelectric starting temperature T_1.

It will be noted that for a brief instant of time upon completion of step **4**, the temperature T_1 of the material **34** remains unchanged, whereas the refrigerant **14** has cooled paraelectrically to a lower temperature T_2. As a result, step **5** occurs in which the material **34** and the colder refrigerant **14** undergo a heat interchange until a thermal equilibrium temperature between the temperatures T_1 and T_2 is reached. Accordingly, the material **34** is cooled by the refrigerant **14**.

Although the instant invention has been described with respect to specific details of a certain embodiment thereof, it is not intended that such details be a limitation upon the scope of the invention except insofar as set forth in the following claims.

I claim:

1. A refrigerator comprising

a paraelectric refrigerant having a rutile-like crystalline lattice structure containing polarizable impurity ions which occupy the bond of said structure that corresponds to the 2.52 A. oxygen-oxygen bond of rutile and whose electric dipole moments are alignable in the *a*—*a* crystal plane,

means for cooling said refrigerant to a starting temperature within its paraelectric refrigeration range,

means for isothermally polarizing said impurity ions while said refrigerant is at said starting temperature in such manner as to align at least a portion of said electric dipole moments and reduce the entropy of said refrigerant, means for thermally isolating said refrigerant, and

means for adiabatically depolarizing said impurity ions while said refrigerant is thermally isolated at said starting temperature, whereby said refrigerant cools paraelectrically.

2. The refrigerator of claim **1** wherein said impurity ions interact under conditions of decreasing temperature to form parallel aligned electric dipole pairs.

3. The refrigerator of claim **1** wherein said polarizable impurity ions are hydroxyl groups.

4. The refrigerator of claim **1** wherein said refrigerant containing polarizable impurity ions is selected from the group consisting of TiO_2, SnO_2, and PbO_2.

5. The refrigerator of claim **1** wherein said means for cooling said refrigerant comprises a cryogenic refrigerator utilizing a cryogenic refrigerant selected from the group consisting of hydrogen and helium.

6. The refrigerator of claim **1** wherein said means for isothermally polarizing said impurity ions comprises

a D.C. electrical potential source connected across said refrigerant in such manner as to produce an electric field therein, and

a switch, series connected between said source and refrigerant whereby said electric field may be applied to said refrigerant as desired.

7. The refrigerator of claim **1** wherein said starting temperature is less than about 20° K.

8. The refrigerator of claim **1** wherein the concentration of said impurity ions in said refrigerant is less than about 10^{21} parts per cubic centimeter.

9. The refrigerator of claim **1** wherein the concentration of said impurity ions in said refrigerant is between about 10^{18} and about 10^{21} parts per cubic centimeter.

10. The refrigerator of claim **1** wherein said means for thermally isolating said refrigerant comprises

a container adapted to house said refrigerant in such manner as to insulate said refrigerant from external thermal influences, said refrigerant being suspended therein by members having negligible heat conduction properties so as to avoid contact with the surfaces of said container, and

vacuum pumping means whereby the atmosphere in said container is effectively removed.

11. A method of refrigeration, the steps of which comprise

cooling a paraelectric refrigerant to a starting temperature within its paraelectric refrigeration range, said refrigerant having a rutile-like crystalline lattice structure containing polarizable impurity ions which occupy the bond of said structure that corresponds to the 2.52 A. oxygen-oxygen bond of rutile and whose electric dipole moments are alignable in the *a—a* crystal plane,

isothermally polarizing said impurity ions while said refrigerant is at said starting temperature in such manner as to align at least a portion of said electric dipole moments and reduce the entropy of said refrigerant,

thermally isolating said refrigerant at said temperature while said impurity ions are polarized, and

adiabatically depolarizing said impurity ions while said refrigerant is thermally isolated at said starting temperature whereby said refrigerant cools paraelectrically.

12. The method of claim **11** wherein said impurity ions interact under conditions of decreasing temperature thereby forming parallel aligned electric dipole pairs.

13. The method of claim **11** wherein said refrigerant containing polarizable impurity ions is selected from the group consisting of TiO_2, SnO_2, and PbO_2.

14. The method of claim **11** wherein said starting temperature is less than about 20° K.

15. The method of claim **11** wherein the concentration of said impurity ions in said refrigerant is less than about 10^{21} parts per cubic centimeter.

16. The method of claim **11** wherein the concentration of said impurity ions in said refrigerant is between about 10^{18} and about 10^{21} parts per cubic centimeter.

17. The method of claim **11** wherein said polarizable impurity ions are hydroxyl groups.

18. A method of refrigerating a material, the steps of which comprise

thermally contacting a material to be cooled with a paraelectric refrigerant, said refrigerant having a rutile-like crystalline lattice structure containing polarizable impurity ions which occupy the bond of said structure that corresponds to the 2.52 A. oxygen-oxygen bond of rutile and whose electric dipole moments are alignable in the *a—a* crystal plane,

cooling said material and refrigerant to a starting temperature within the paraelectric refrigeration range of said refrigerant,

isothermally polarizing said impurity ions while said refrigerant is at said starting temperature in such manner as to align at least a portion of said electric dipole moments and reduce the entropy of said refrigerant,

thermally isolating said material and refrigerant, said refrigerant being in thermal contact with said material at said starting temperature, while said impurity ions are polarized, and

adiabatically depolarizing said impurity ions while said refrigerant and material are thermally isolated at said starting temperature whereby said refrigerant cools paraelectrically and thereby cools said material by heat conduction therebetween.

19. The method of claim **18** wherein said impurity ions interact under conditions of decreasing temperature thereby forming parallel aligned electric dipole pairs.

20. The method of claim **18** wherein said refrigerant containing polarizable impurity ions is selected from the group consisting of TiO_2, SnO_2, and PbO_2.

21. The method of claim **18** wherein said starting temperature is less than about 20° K.

22. The method of claim **18** wherein the concentration of said impurity ions in said refrigerant is less than about 10^{21} parts per cubic centimeter.

23. The method of claim **18** wherein the concentration of said impurity ions in said refrigerant is between about 10^{18} and 10^{21} parts per cubic centimeter.

24. The method of claim **18** wherein said polarizable impurity ions are hydroxyl groups.

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WILLIAM J. WYE, *Primary Examiner.*