United States Patent

Lawless

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[54] CLOSED-CYCLE ELECTROCALORIC REFRIGERATOR AND METHOD

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[51] **Int. Cl.** **F25b 21/02**
[58] **Field of Search** 62/3

[56] **References Cited**

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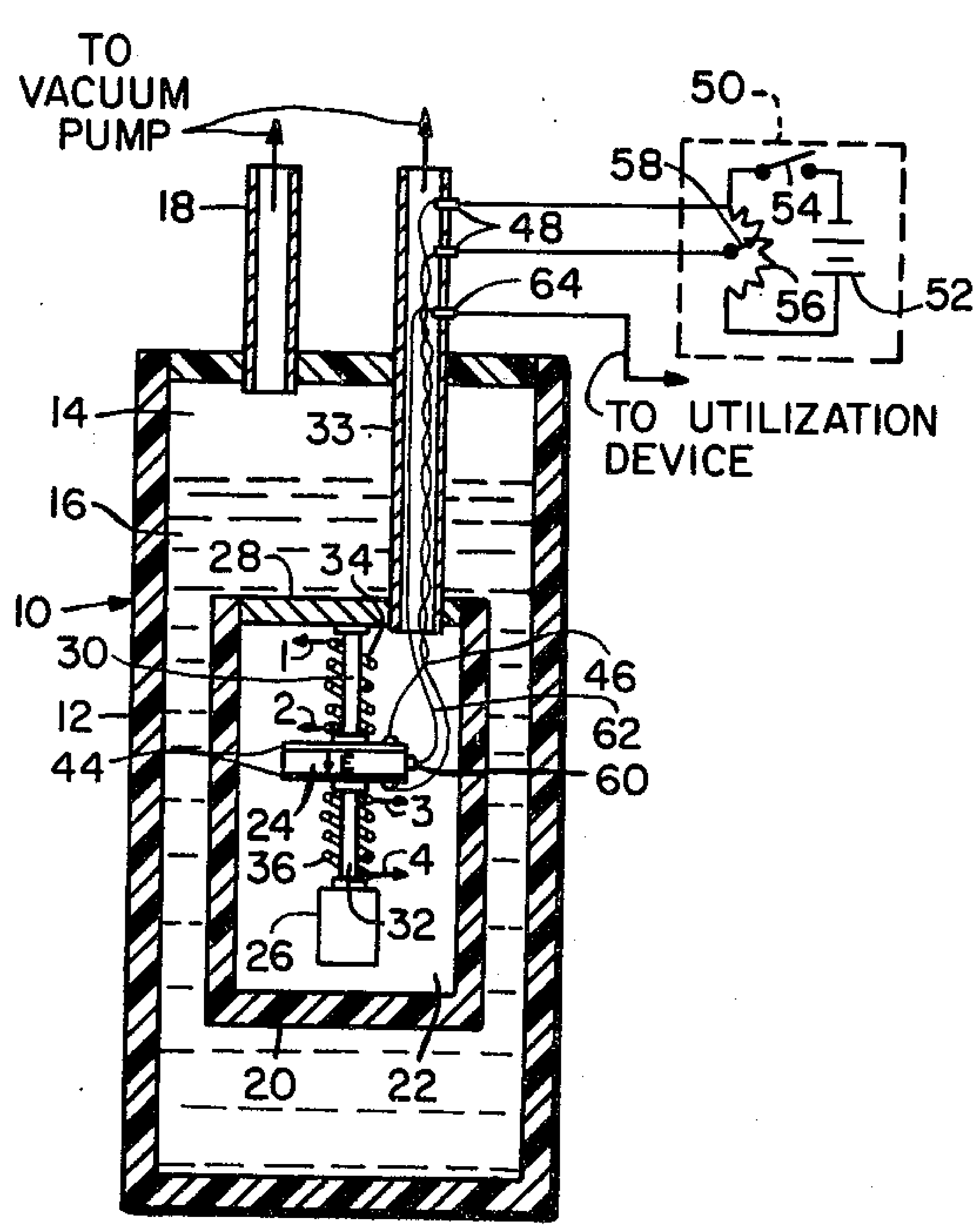
[57] **ABSTRACT**

A closed-cycle solid state refrigerator is disclosed that is capable of accurately and efficiently achieving extremely low temperatures. A second stage of the refrigerator comprises an evacuated chamber in which is disposed a solid state refrigerant that is connected by a first thermal valve to a first stage such as a cryostat and by a second thermal valve to a heat generating load that is to be cooled. The refrigerant consists of a polarizable electrocaloric material, the entropy of which can be substantially reduced by changing an electric field set up therein by a pair of electrodes disposed on opposite sides thereof. The refrigerant and the load are cooled by cycling the refrigerator through a given sequence of steps including opening and closing the thermal valves and changing the value of the applied electric field.

22 Claims, 4 Drawing Figures



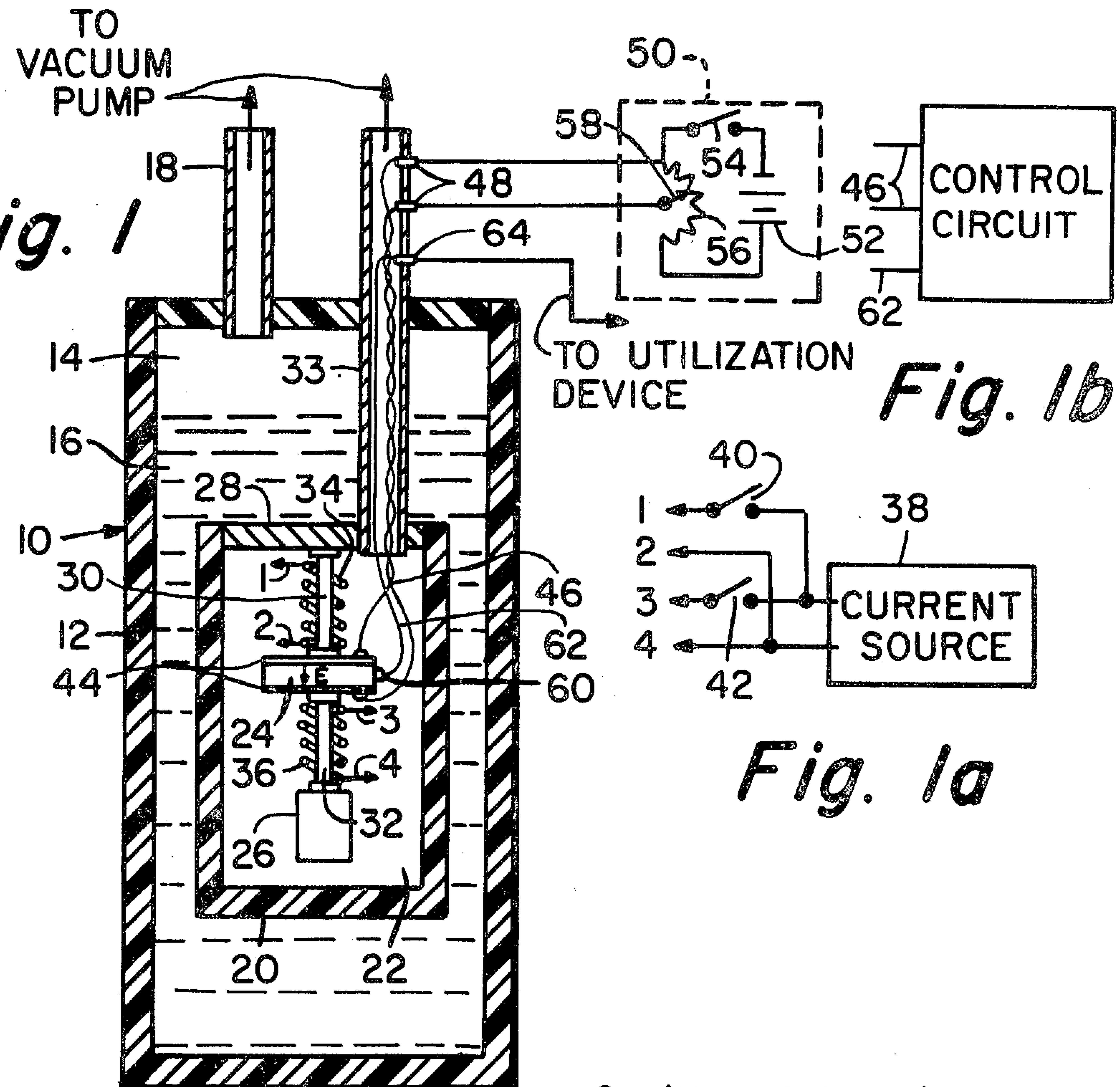


Fig. 1

Fig. 1a

Fig. 1b

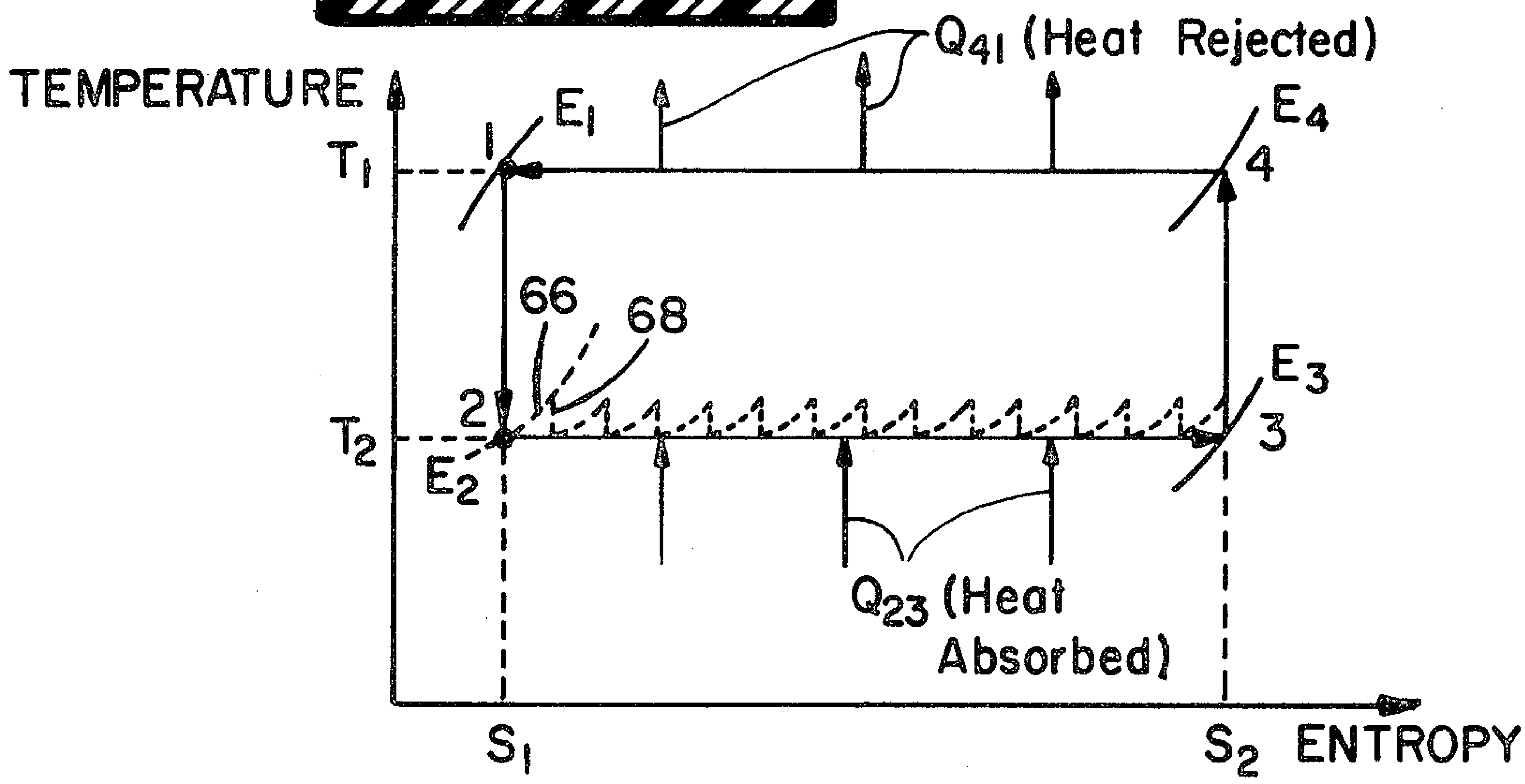


Fig. 2

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CLOSED-CYCLE ELECTROCALORIC REFRIGERATOR AND METHOD

BACKGROUND OF THE INVENTION

The development in recent years of devices and systems which function at cryogenic temperatures, such as cryogenic computer memories, high efficiency gallium arsenide diodes, high-field superconducting alloys, masers, and the like has led to a search for more economical and less complex means for obtaining cryogenic environments. To achieve temperatures on the order of 1° K., 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 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 0.02° 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 complex helium refrigeration systems.

In my U.S. Pat. No. 3,436,924 entitled "Paraelectric Refrigeration Method and Apparatus" there is disclosed a paraelectric refrigerator which utilizes a solid-state refrigerant that cools paraelectrically from a starting temperature as high as about 20° K. Electrodes are disposed on opposite sides of the paraelectric refrigerant, and a load disposed adjacent one of the electrodes is in thermal contact with the refrigerant. A cryogenic refrigerant is introduced into a chamber containing the above-described assembly which is thereby cooled to within the paraelectric cooling range of the paraelectric refrigerant which is then isothermally polarized by an applied electric field. The refrigerant and load are then thermally isolated by evacuating the chamber and the refrigerant is caused to cool paraelectrically by adiabatically depolarizing the paraelectric refrigerant by removing the applied electric field. Although the system of said patent is capable of providing paraelectric cooling from a starting temperature as high as about 20° K., the efficiency of operation of said system is low and the final temperature to which the refrigerant and load are ultimately cooled is not easily controlled.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a refrigerator capable of accurately refrigerating a load at a preselected temperature.

Another object of the present invention is to provide a refrigerator that is capable of cooling in a manner which is more efficient than has been heretofore possible.

Another object of the present invention is to provide a refrigeration method for accurately and efficiently refrigerating a load.

Briefly, the present invention relates to a closed-cycle refrigerator for refrigerating a mass of material. This refrigerator includes an electrocaloric refrigerant and a sink for absorbing heat from the refrigerant at a substantially constant temperature within the electrocaloric refrigeration range of the refrigerant. Valve means are provided for thermally connecting and separating the refrigerant and the material to be cooled and also for thermally connecting and separating the refrigerant and sink. Means are provided for isolating the refrigerant and the material, and means are provided for electrically polarizing and depolarizing the refrigerant.

This refrigerator functions in accordance with the following process. The refrigerant and material to be refrigerated are thermally connected to the heat sink, the temperature of which is T_1, so that the refrigerant and the material are substantially cooled to temperature T_1. Then, after thermally isolating the material, the polarization of the refrigerant is isothermally changed toward a first state of polarization by applying thereto an electric field of intensity E_1 to reduce the entropy of the refrigerant to a value S_1. The refrigerant is then thermally isolated, and the polarization thereof is adiabatically changed toward a second state of polarization opposite the first state by changing the intensity of the field from intensity E_1 to an intensity E_2 to reduce the temperature of the refrigerant from temperature T_1 to a temperature T_2. The refrigerant is then thermally connected to the material to decrease the temperature thereof below the temperature T_1.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 1*a* show an elevation view of a closed-cycle electrocaloric refrigeration system with associated control circuitry illustrating one embodiment of the present invention.

FIG. 1*b* illustrates an alternate embodiment of the control circuitry of the present invention.

FIG. 2 is a graph of the temperature vs. entropy characteristics of a solid-state material employed as a refrigerant in the system of FIGS. 1 and 1*a* during a typical Carnot-cycle operating sequence.

DETAILED DESCRIPTION

The solid state, closed-cycle refrigerator of the present invention is capable of cooling by either of two operating cycles depending upon whether the electrocaloric material utilized therein cools upon the adiabatic depolarization thereof (type I materials or paraelectric materials) or the adiabatic polarization thereof (type II materials). Since the type I materials are more conventional, the operation of the invention will first be described with reference to such type I or paraelectric materials.

As used herein, an electrocaloric refrigerant is a material the temperature of which changes, under adiabatic conditions, in response to the application of an electric field. This means that the entropy of the material is controlled externally by polarization and depolarization of the material. An electrocaloric refrigerator is defined as one which employs an electrocaloric refrigerant. As used herein, the electrocaloric refrigeration range is that range of temperatures for which entropy of an electrocaloric material is substantially reduced by changing the polarization of the material by an applied electric field. This means that the amount of entropy decrease should be about as large as the total entropy in the absence of the polarizing field. The electrocaloric starting temperature is defined as any temperature within the electrocaloric refrigeration range.

Referring to FIG. 1 there is shown an example of the closed-cycle electrocaloric refrigeration system of the present invention. A first stage of two refrigeration stages of the system consists of a conventional helium cryostat **10** which is employed to provide the necessary electrocaloric starting temperature, and to act as a high temperature isothermal heat sink during closed-cycle operation. Cryostat **10** consists of a pressure vessel **12** having a vacuum chamber **14** which, under the usual operating conditions, contains a quantity of liquid helium **16**. A pipe **18** communicating with chamber **14** may be employed to introduce helium into the chamber, and by connecting it to a suitable vacuum pump, not shown, provides means whereby a partial vacuum may be drawn on chamber **14** if desired. Any suitable and well-known type of cryogenic refrigerator, having the capacity to attain the desired electrocaloric starting temperature, may be used in place of cryostat **10**. Examples of suitable substitutes include the well-known Stirling-cycle refrigerator, the Gifford-McMahon cycle refrigerator, a helium dilution refrigerator, and the like.

The second stage of the system is an electrocaloric refrigeration stage consisting of pressure vessel **20** having an overall size suitable for suspension within chamber **14**. Under operating conditions of the first stage, it is preferable that vessel **20** be completely immersed in the liquid helium **16** as shown. Vessel **20** also has a vacuum chamber **22** in which is suspended any suitable electrocaloric refrigerant **24**, and a mass of any material, hereinafter referred to as a thermal load **26**, which material is to be refrigerated by the system in accordance with the process of the present invention. Note that the load is a source of heat, and this heat is to be absorbed so as to keep the load temperature constant. Refrigerant **24** is suspended from a thermally conductive lid **28**, so as not to contact the defining walls of the chamber **22**, by means of a conventional superconductive thermal switch or valve **30**. The load **26** is similarly suspended from the refrigerant **24** by means of a second thermal valve **32**, preferably of the same type as valve **30**. A pipe **33**, communicating with chamber **22**, can be connected to a suitable vacuum pump, not shown, in order that a high quality vacuum, preferably on the order of about 1 micron of Hg or less, can be drawn on chamber **22** during the operating sequence of the system. Such a vacuum level insures that the materials within chamber **22** can be effectively thermally isolated from chamber **14** when the refrigeration process of the present invention so requires. A lower quality vacuum may be employed successfully, however, the quality of thermal isolation obtainable, and, hence, the refrigeration efficiency of the system may be expected to suffer as a result. The load and refrigerant could also be thermally isolated by filling the space between these elements and the inner walls of the chamber with an insulating material.

Those skilled in the art will appreciate that the superconductive thermal valves **30** and **32** undergo a transition to a superconducting state at a suitable low temperature, but the application of a magnetic field can drive this type of material back into the nonsuperconducting or normal state. Since the superconducting state has a very low thermal conductivity relative to the normal state, a thermal valve property is produced. Magnetic coils **34** and **36** surround the valves **30** and **32**, respectively.

Referring additionally to FIG. 1*a*, an electric current source **38** is connected through switch **40** across coil **34** as indicated by match lines labeled **1** and **2**, and through a switch **42** across coil **36** as indicated by match lines labeled **3** and **4**. As long as switches **40** and **42** are in the open position as shown, no magnetic fields are generated by coils **34** and **36**, and valves **30** and **32** will remain in a state of low thermal conductivity so long as their temperature is below the superconducting transition temperature. The thermal conductivity of valves **30** and **32** can be rendered normal by closing switches **40** and **42** to magnetically energize coils **34** and **36** respectively. The state of thermal conductivity of each of the valves **30** and **32** should be controllable independent of the conductive state of the other, as is the case in the present example.

To obtain electrocaloric refrigeration effects with Type I materials, it is necessary to polarize at least a portion of the polarizable agents of refrigerant **24** with an electric field, the existence of which field is represented by an arrow labeled E. To accomplish this, a pair of spaced plate or film electrodes **44** are disposed on opposite surfaces of the refrigerant **24** to form a capacitorlike assembly. Electrodes **44** are electrically connected by lead wires **46** which pass through a pair of feedthrough insulators **48**, to an adjustable high voltage supply **50**.

Supply **50** may be of any well-known type capable of providing a voltage across electrodes **44** and consequently, an electric field E through refrigerant **24** of sufficient intensity to at least partially polarize the latter. For example, the supply **50** may consist of a DC voltage source **52** connected by means of an enabling switch **54** across a suitable voltage dividing network **56**. The voltage applied across the electrodes **44** is taken from the network **56** between one side thereof and an adjustable tap or contact **58**. By adjusting contact **58**, it is possible to reduce the voltage across electrodes **44** from a maximum value equal to the voltage across source **52**, to 0 volts.

In order to monitor the temperature of refrigerant **24** during the operating sequence, a thermometer **60**, such as the well-known germanium resistance type, may be used. A lead wire **62** from thermometer **60** may be brought through pipe **33** and feedthrough insulator **64** where it may be connected to any suitable utilization device, not shown, for temperature display and control purposes. Alternately, the refrigerant may be used as its own thermometer, as for example, by measuring the capacitance across electrodes **44**. The high-voltage supply could consist of a conventional control circuit **65** which provides an output voltage to maintain the refrigerant at temperature T_1 in which case lead wire **62** would be connected directly to the voltage supply as illustrated in FIG. 1*b*.

Referring now to FIGS. **1** and **2**, a typical Carnot-cycle operating sequence of the system of the present invention will be explained in connection with Type I materials. Although numerous other operating modes may be employed, the Carnot-cycle mode of operation is preferred since its use yields the highest possible thermodynamic efficiency for any selected set of operating temperatures.

Assume that the system of FIG. **1** is initially at room temperature with all the switches **40**, **42**, and **54** in an open position as shown. It will therefore be necessary to establish certain initial conditions within the system before the operating sequence can begin. First, a suitable starting temperature T_1 must be selected which is within the electrocaloric refrigeration range of refrigerant **24**. This selection will depend partly upon the physical nature of the particular electrocaloric material employed as refrigerant **24**, and partly upon the ultimate low temperature T_2 desired to be obtained. Although most useful Type I electrocaloric materials show some slight tendency to cool paraelectrically at relatively high temperatures (100° K.), it will probably be found necessary to start the process from a much lower temperature, preferably in the range of pumped liquid helium below 1.5° K., where a substantial percentage temperature decrease can be obtained. For Type I materials the reduction in entropy by changing the polarization of such material assures that the temperature of the material will drop by a substantial percentage when the material is subsequently depolarized adiabatically. The Type I electrocaloric materials whose properties have been fairly thoroughly investigated include polar impurity doped alkalihalides such as NaCl:OH, KCl:OH, RbCl:CN, and the like and polar impurity doped rutilelike crystalline material such as TiO_2:OH, SbO_2:OH, and the like.

Since the paraelectric properties of KCl:0H appear to be well understood in the art at the present time, this material has been selected for refrigerant **24** of the present example for the purpose of illustrating the use of Type I electrocaloric materials. However, it should be mentioned that any of the abovementioned or other suitable Type I materials can be used successfully in the present invention. Provided they are doped with a polar impurity to within a reasonable range of concentrations, each will produce a substantial temperature decrease paraelectrically when the process is begun from a starting temperature T_1 within the range of liquid helium.

A suitable starting temperature T_1 having been selected, refrigerant **24**, consisting of about 20 cc. of KC1 containing about 10^{18} OH ions/cc., load **26** and valves **30** and **32** are refrigerated by refrigerator **10** since a heat conductive path extends from helium **16** through lid **28**, valve **30**, refrigerant **24**, and valve **32** to the load. It may be found desirable to pump a gas such as helium into chamber **22** to improve thermal contact between the articles within chamber **22** and helium **16** by way of thermally conductive lid **28** during this cooling step. Once the assembly within the chamber **22** is brought into thermal equilibrium with helium **16** at the desired starting temperature T_1, chamber **22** is evacuated, preferably to about 1 micron of Hg or less, in order to provide conditions wherein refrigerant **24** and load **26** can be effectively isolated thermally when required during the operating sequence to follow.

Valves 30 and 32, then being at an operative temperature, can be utilized as required to provide the necessary thermal connections between refrigerant 24, load 26, and helium 16.

With refrigerant 24 at the desired starting temperature T_1, switch 40 may be closed to provide thermal contact between helium 16 and the refrigerant under the evacuated condition of the chamber 22. Then switch 54 is closed and contact 58 is adjusted so as to apply a potential to electrodes 44 thereby generating a field E, preferably of sufficient intensity E_1 to align substantially all of the polarizable agents contained in the Type I refrigerant 24, this condition being known as saturation polarization. The symbols E_1, E_2, E_3, and E_4 are situated adjacent to equipotential lines passing through points 1, 2, 3, and 4, respectively. Though an intensity E_1 of less than that necessary to produce saturation polarization may be used, either the operating temperature difference will be reduced or the period during which T_2 can be maintained (line segment 2–3) will be reduced. Using the refrigerant of the present example, an electric field intensity E_1 of about 60 kv./cm. will be sufficient to produce the desired state of saturation at about 1.3° K. in KCl:OH. A greater intensity E_1 could be employed up to the dielectric breakdown strength of refrigerant 24, but this could not produce a higher level of polarization and therefore would not result in any greater operating advantage.

Immediately after the field E is applied, a heat of polarization is generated within refrigerant 24. However, since refrigerant 24 is thermally connected to helium 16 by valve 30, the heat of polarization will be absorbed by the helium and the polarization step will be brought about in a substantially isothermal manner. Accordingly, the entropy of refrigerant 24 will be substantially reduced below that of its unpolarized condition, to an entropy of S_1. The initial conditions S_1, E_1, and T_1 of the refrigerant 24, as represented by the point 1 in FIG. 2, are now established so that the operating sequence of the system can begin. Switch 40 should now be opened to thermally isolate refrigerant 24 from helium 16.

Refrigerant 24 is thereafter partially depolarized by adjusting contact 58 to reduce field E from intensity E_1 to a lower intensity E_2 (greater than 0 volts/cm.). In general, the lower the intensity E_2, the lower will be the final temperature T_2 to which refrigerant 24 will cool, so long as refrigerant 24 remains within its electrocaloric refrigeration range. The low temperature limit attainable will be in the fraction of a degree Kelvin range where quantum effects known in the art as zero field splitting effects become appreciable.

It is advantageous to only partially depolarize refrigerant 24 rather than completely depolarize it, since by partial depolarization, as by adjusting contact 58, the final temperature T_2 can be selected quite accurately. Also, refrigerant 24 can be employed at the heart of a Carnot-cycle refrigeration system because the residual intensity E_2 remaining after partial depolarization can be advantageously employed to maintain isothermal conditions by offsetting the effects of heat leakage into refrigerant 24 from heat generated in the load, for example.

Refrigerant 24, having been partially depolarized, will cool adiabatically along the line segment 1–2 as thermal energy within refrigerant 24 is converted into potential energy during the disalignment of a quantity of the polarizable agents within the refrigerant material refrigerant material relative to the direction of the field E. Equilibrium conditions will be established and the condition of refrigerant 24 will stabilize at point 2. Starting from point 1 under saturation conditions of about 60 kv./cm. at a temperature T_1 of about 1.3° K. it should be possible to cool refrigerant 24 by partial adiabatic depolarization to a final temperature T_2 of about 0.1° K. with an electric field intensity E_2 of about 8.0 kv./cm. remaining. However, some adjustment in the intensity E_2 may be required in order to attain the precisely desired final temperature T_2.

Now refrigerant 24 is at the final temperature T_2, and assuming the first cycle of operation of the system is being executed, load 26 is still at the starting temperature T_1, since valve 32 is still closed. At this point in later successive cycles of operation, however, the temperature of load 26 will approach and reach temperature T_2, after which time the operation of the refrigerator is to maintain the load at T_2.

To cool load 26, switch 42 is closed to thermally connect load 26 and refrigerant 24. Accordingly, refrigerant 24 begins absorbing heat from the warmer load thus tending to reduce the temperature of the latter. For maximum thermodynamic efficiency, it is important that refrigerant 24 absorb heat from load 26 in a substantially isothermal manner so that the entropy of refrigerant 24 will increase along the line segment 2–3 until thermal equilibrium is eventually established at the point 3. Clearly, however, without taking additional measures, the temperature of refrigerant 24 will tend to increase as it absorbs heat thus departing from the desired operating path to follow a curve of constant field intensity E_2 as represented by the dashed curve 66. To correct this tendency, contact 58 is adjusted as soon as a slight temperature increase is detected by the thermometer 60 so as to reduce the field E by a sufficient increment to return refrigerant 24 to the desired temperature T_2. The dashed line segment 68 represents the slight decrease in temperature of refrigerant 24 brought about by this incremental or partial depolarization. From time-to-time further reductions in the field E should be made to offset the continuing effect of heat absorption by refrigerant 24. This can readily be accomplished either manually by observing the temperature of refrigerant 24, or automatically through the use of any well-known temperature responsive automatic control means. In either case the line segment 2–3 can be adhered to quite closely so that an excellent quality Carnot-cycle sequence can be approached. Eventually the field will be reduced to zero and point 3 will be reached. In the time period that elapses during the portion of the cycle represented by line segment 2–3, the refrigerant absorbs heat from the load, and this condition is represented by the arrows labeled Q_{23}.

Ideally there should have been just enough field intensity at point 2 to have been completely expended along the line segment 2–3 such that the field E_3 at point 3 is zero. Though this would be desirable in improving the refrigeration capacity of the system, it is not essential to the success of the process. Therefore, some quantity of field E could exist at the point 3 as represented by E_3.

The load 26 is then thermally isolated from refrigerant 24 by opening switch 42, and contact 58 is adjusted to increase the intensity of the field to a value E_4 just sufficient to increase the temperature of refrigerant 24 to the starting temperature T_1. In effect refrigerant 24 is now being repolarized so that its temperature increases as the heat of polarization is generated. The step is adiabatic since it will be observed that refrigerant 24 is in a thermally isolated condition at this time, both the valves 30 and 32 being in a nonconductive condition.

When the field has been increased to a value E_4 so that the temperature of refrigerant 24 is at T_1, refrigerant 24 is thermally connected to helium 16 by closing switch 40 and energizing valve 30 to a state of high thermal conductivity. Since both refrigerant 24 and helium 16 are at the same temperature T_1 no heat transfer will take place as a result. However, now contact 58 is further adjusted to increase the intensity of field E from E_4 to the saturation intensity E_1. Since refrigerant 24 is now thermally connected to helium 16 the heat of polarization is absorbed by the latter and the step occurs isothermally at the starting temperature T_1 along line segment 4–1. The arrows labeled Q_{41} point away from line segment 4–1 to represent the heat rejected by the refrigerant. Equilibrium conditions are established at point 1, the initial cycle of operation of the system being completed, and a similar new cycle can now begin.

It should be noted that where the thermal insulation of the system is high, and where the load does not generate heat, it may not be necessary to begin a new refrigeration cycle immediately. The maximum permissable time lapse between the end of a cycle and the beginning of a succeeding cycle will depend on the rate of heat leakage into the system and the rate of heat generated by the load, if any. Consequently, the time lapse between cycles depends on how rapidly load **26** tends to increase in temperature from the desired value T_2. If the load were a source of heat, the system could be operated in a continuous series of cycles, one immediately following another, as is commonly the case with many well-known closed-cycle refrigerators.

The refrigerator of FIGS. **1** and **1***a* can operate in a cycle different from that described above when Type II materials are utilized. However, reference may still be made to FIG. **2** for a description of this modified operating cycle, since only the valves of the electric field intensities E_1, E_2, E_3 and E_4 are changed. A family of electrocaloric materials has been discovered that functions as Type II materials, i.e., the materials cool when adiabatically polarized. These materials are strontium titanate-containing glasses from which the strontium titanate, for example pervoskite strontium titanate, has been controllably crystallized, and results in a body composed of a multiplicity of uniform very fine grain crystals substantially homogenously dispersed in a glassy matrix and forming a large proportion thereof. Such materials can be obtained when at least 50 percent by weight of strontium titanate, including 0 to 5 percent by weight of dopants, is melted into a glass at a temperature of about 1,650° C., and a low-temperature ferroelectric strontium titanate can be subsequently crystallized in this glass upon reheating between 800° and 1,300° C., for a time period of at least one hour at 800° C. and at least ½ minute at 1,300° C. A more complete discussion of a suitable heat treatment process used for the formation of crystals may be found in the A. Herczog and S. D. Stookey patent, U.S. Pat. No. 3,195,030 which is incorporated herein by reference. With proper heat treatment, strontium titanate is the major crystallized phase that will result. It is to be understood that said glass can be heat treated prior to use in or formation of an ultimate device, or such device may be formed using the glass and thereafter be subjected to heat treatment whereby the strontium titanate is crystallized in situ. Small additions of up to 5 percent by weight may be made of oxides such as niobium oxide, tantalum oxide, vanadium oxide and bismuth oxide. Such dopants tend to stabilize the titanate phase. Suitable glasses for forming the glass matrix of the present invention may be alumino-silicate, borate, phosphate, or germanite glasses.

Table I represents examples of compositions on a batch basis in percent by weight which, when heat treated as herein set forth, provide material comprising strontium titanate crystals in a glass matrix suitable for the purposes of the present invention.

TABLE I

Ex.	$SrTiO_3$	$SrCO_3$	TiO_2	SiO_2	Al_2O_3	Nb_2O_5	V_2O_5	Ta_2O_5	Bi_2O_5
1		49.4	26.7	19.9	4.0				
2	72.0			18.7	9.3				
3	57.8	12.5		21.1	8.6				
4	68.4	0.6		20.0	10.0	1.0			
5	62.8	2.7		19.8	9.9	4.8			
6		47.8	25.1	21.5	4.3	1.7			
7	68.4	0.6		20.0	10.0		1.0		
8	62.8	2.7		19.8	9.9		4.8		
9		47.4	25.1	21.5	4.3		1.7		
10	68.4	0.6		20.0	10.0			1.0	
11	62.8	2.7		19.8	9.9			4.8	
12		47.4	25.1	21.5	4.3			1.7	
13	68.4	0.6		20.0	10.0				1.0
14	62.8	2.7		19.8	9.9				4.6
15		47.4	25.1	21.5	4.3				1.7
16		50.4	27.3	18.6	3.7				
17		50.1	27.1	19.0	3.8				
18		47.9	25.9	17.5	8.7				
19		49.1	26.6	19.4	4.9				

With a Type II material refrigerant incorporated in the refrigerator of FIGS. **1** and **1***a*, the operation of the refrigerator is similar to that described in connection with Type I refrigerants, except as follows. Initial conditions are established at point **1** of FIG. **2** by reducing the temperature of refrigerant **24** and load **26** to temperature T_1 as described above, but the entropy of refrigerant **24** is reduced by reducing the electric field therein to zero. If this is the initial cycle of operation the zero field state in which the Type II material naturally exists will merely be maintained. With both valves **30** and **32** closed so that no heat flows to or from the refrigerant, the electric field applied to the Type II refrigerant is increased from its zero value to an intermediate value, causing the temperature of the refrigerant to drop from temperature T_1 to a preselected lower temperature T_2. This condition is represented by point **2** on the curve of FIG. **2**. Valve **32** is then opened so that heat can flow from the load to the refrigerant. As heat is absorbed by the refrigerant the temperature thereof increases and the temperature-entropy relationship starts to follow curve **66**. Since maximum efficiency is obtained when the operating cycle is caused to follow line segment **2–3**, the field intensity is increased slightly as soon as a slight temperature increase is detected by the thermometer **60** so that the temperature of refrigerant **24** is again reduced to the desired temperature T_2. The dashed line segment **68** represents the slight decrease in temperature of refrigerant **24** brought about by this incremental polarization resulting from the increased electrical field E. Further increases in the field are made as necessary to offset any tendency of the refrigerant to sustain a temperature increase as it absorbs heat from the load represented by arrows Q_{23}. As in the previous description, the temperature-entropy relationship can be caused to follow line segment **2–3** by observing or sensing the temperature of the refrigerant as measured by thermometer **60** and then appropriately increasing the voltage applied to electrodes **44**. The refrigerant can thereby be maintained at a temperature T_2 until saturation polarization is reached at a maximum electric field E_3. In FIG. **2**, this condition is represented by point **3**. An increase in field intensity above saturation intensity E_3 cannot produce any further entropy change.

Switch **42** is now opened to thermally isolate load **26** from refrigerant **24**. With both valves **30** and **32** closed, the field is decreased to a value E_4 to warm the refrigerant to the first-stage temperature T_1. This adiabatic temperature increase follows line segment **3–4**. Valve **30** is then opened so that heat can flow between the refrigerant and the first-stage, and the electric field on the refrigerant is isothermally decreased to zero. During this step heat, represented by arrows Q_{41}, flows from the refrigerant to the first-stage and the temperature of the refrigerant is maintained constant at T_1. Equilibrium conditions are thereby again established at point **1** and another cycle can be started.

Although the present invention has been described with respect to specific details of certain embodiments thereof, it is not intended that such details be limitations on the present invention. Although maximum efficiency is obtained by causing the apparatus of the present invention to operate on a Carnot-cycle, this invention encompasses any closed-cycle type of operation. For example, after the refrigerant cools to temperature T_2 at point **2** of FIG. **2**, and load **26** is connected thereto, the temperature of the refrigerant could be permitted to increase along dashed line **66** until temperature T_1 is reached. Thereafter, field E_1 could be established and the refrigerant could be connected to the first stage by valve **30** to bring the system back to the initial condition at point **1**. Another modification in the operating cycle could be achieved by simultaneously applying field E_1 to the refrigerant while opening valve 30 after the operating cycle has progressed along line segments 1–2 and 2–3 of FIG. 2. The result would be to move from point 3 to point 1. It is obvious that there are many other modes of operation too numerous to mention, but which are within the scope of the following claims.

I claim:

1. A closed-cycle process for refrigerating a mass of material comprising the steps of
   - providing an electrocaloric refrigerant,
   - thermally connecting said refrigerant and material to a sink having a temperature of T_1 so that said refrigerant and material are substantially cooled to temperature T_1,
   - thermally isolating said material,
   - isothermally changing the polarization of said refrigerant toward a first state of polarization by applying thereto an electric field of intensity E_1 to reduce the entropy of said refrigerant to a value S_1, the condition of said refrigerant wherein the entropy thereof is at value S_1, the temperature thereof is at value T_1, and the electric field applied thereto is of value E_1 constituting an initial condition,
   - thermally isolating said refrigerant,
   - adiabatically changing the polarization of said refrigerant to a second state of polarization by changing the intensity of said field from said intensity E_1 to an intensity E_2 to reduce the temperature of said refrigerant from said temperature T_1 to a temperature T_2, and
   - thermally connecting said refrigerant to said material to decrease the temperature of said material.

2. The process of claim 1 wherein, after the step of thermally connecting said refrigerant to said material, said initial condition is reestablished.

3. The process of claim 2 wherein said step of reestablishing said initial condition comprises changing said field from said intensity E_2 to an intensity E_3 such that said refrigerant absorbs heat from said material substantially isothermally and the entropy of said refrigerant increases from said value S_1 to a value S_2, said change in field intensity from E_2 to E_3 being in the same direction as the change in field intensity from E_1 to E_2.

4. The process of claim 3 wherein said step of reestablishing said initial conditions further comprises
   - adiabatically changing said field intensity to an intensity E_4, said change in field intensity from E_3 to E_4 being in the direction opposite to the change in field intensity from E_1 to E_2, to increase the temperature of said refrigerant from said temperature T_2 to said temperature T_2, and
   - isothermally changing said field from said intensity E_4 to said intensity E_1 to reduce the entropy of said refrigerant from said value S_2 to said value S_1.

5. The process of claim 4 wherein said field intensity E_1 is sufficiently high to substantially produce saturation polarization of said refrigerant and said field intensity E_3 is substantially 0.

6. The process of claim 4 wherein said field intensity E_1 is substantially 0.

7. The process of claim 1 wherein said refrigerant is a material selected from the group consisting of electrically polar ion doped alkali-halides, electrically polar ion doped rutilelike crystalline materials, and glass ceramics consisting of a glass matrix, 0 to 5 percent by weight of at least one dopant, and at least 50 percent by weight of strontium titanate, wherein at least a portion of said strontium titanate is crystallized.

8. A closed-cycle refrigerator for refrigerating a mass of material, said refrigerator comprising
   - an electrocaloric refrigerant,
   - a sink for absorbing heat from said refrigerant at a substantially constant temperature within the electrocaloric refrigeration range of said refrigerant,
   - means for thermally connecting and separating said refrigerant and said material,
   - means for thermally connecting and separating said refrigerant and sink,
   - means for thermally isolating said refrigerant and material when said last recited means thermally separate said refrigerant and sink, and
   - means for electrically polarizing and depolarizing said refrigerant.

9. The refrigerator of claim 8 wherein said refrigerant consists essentially of a host crystalline material containing a polar ion dopant selected from the group consisting of OH and CN ions.

10. The refrigerator of claim 8 wherein said refrigerant consists of a material selected from the group consisting of electrically polar ion doped alkali-halides, electrically polar ion doped rutilelike crystalline materials, and glass ceramics consisting of a glass matrix, 0 to 5 percent by weight of at least one dopant, and at least 50 percent by weight of strontium titanate, wherein at least a portion of said strontium titanate is crystallized.

11. The refrigerator of claim 8 wherein said sink comprises a helium cryogenic refrigerator.

12. The refrigerator of claim 8 wherein said means for thermally connecting and separating said refrigerant and sink comprises a first magnetically actuated thermal valve connected between said refrigerant and sink.

13. The refrigerator of claim 8 wherein said means for thermally connecting and separating said refrigerant and material comprises a second magnetically actuated thermal valve connected between said refrigerant and material.

14. The refrigerator of claim 8 wherein said means for thermally isolating comprises a vacuum chamber in which said refrigerant and material are disposed.

15. The refrigerator of claim 8 wherein said means for polarizing and depolarizing said refrigerant comprises
   - a variable high-voltage source, and
   - a pair of electrodes separated by said refrigerant, said electrodes being connected across said source.

16. The refrigerator of claim 8 further comprising
   - means for detecting the temperature of said refrigerant, and
   - means responsively connected to said detecting means for changing the polarization of said refrigerant in response to a temperature rise therein, for maintaining said refrigerant at a substantially constant temperature while said refrigerant absorbs heat from said material.

17. The refrigerator of claim 12 wherein said means for thermally connecting and separating said refrigerant and material comprises a second magnetically actuated thermal valve connected between said refrigerant and material, and wherein said means for polarizing and depolarizing said refrigerant comprises a high-voltage source and a pair of electrodes separated by said refrigerant, said electrodes being connected across said high-voltage source.

18. The refrigerator of claim 17 wherein said means for thermally isolating comprises a vacuum chamber in which said refrigerant and material are disposed.

19. The refrigerator of claim 18 wherein said refrigerant consists essentially of a host crystalline material containing a polar ion dopant selected from the group consisting of OH and CN ions.

20. The refrigerator of claim 19 wherein said sink comprises a helium cryogenic refrigerator.

21. The refrigerator of claim 18 wherein said refrigerant consists of a material selected from the group consisting of electrically polar ion doped alkali-halides, electrically polar ion doped rutilelike crystalline materials, and glass ceramics consisting of a glass matrix, 0 to 5 percent by weight of at least one dopant, and at least 50 percent by weight of strontium titanate, wherein at least a portion of said strontium titanate is crystallized.

22. The refrigerator of claim 21 wherein said sink comprises a helium cryogenic refrigerator.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,638,440 Dated February 1, 1972

Inventor(s) William N. Lawless

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, Table 1, Example 6, "47.8" should be -- 47.4 --; Example 14, "4.6" should be -- 4.8 --.

Claim 4, line 7, "T_2" (second occurrence) should be -- T_1 --.

Signed and sealed this 1st day of August 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents