(19) World Intellectual Property Organization International Bureau



T TERRE BUILDER IN BERKE HER BERKE BERKE BERKE BUILD BUILD

(43) International Publication Date 7 June 2007 (07.06.2007)

(10) International Publication Number WO~2007/064352~A1

(51) International Patent Classification: *G01R 33/3415* (2006.01)

19711 (US). MCCAMBRIDGE, James, D. [US/US]; 406 Walnut Lane, Swarthmore, Pennsylvania 19081 (US).

(21) International Application Number:

PCT/US2006/015460

(74) Agent: MEDWICK, George, M.; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(22) International Filing Date:

24 April 2006 (24.04.2006)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

11/118,962

29 April 2005 (29.04.2005) US

(71) Applicant (for all designated States except US): E. I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

- tarket Street, Willington, Delaware 17676
- (72) Inventors; and
 (75) Inventors/Applicants (for US only): ALVAREZ, Robby,
 L. [US/US]; 70 Hidden Valley Drive, Newark, Delaware
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: SCANNING A BAND OF FREQUENCIES USING AN ARRAY OF HIGH TEMPERATURE SUPERCONDUCTOR SENSORS TUNED TO THE SAME FREQUENCY

















†2

(57) Abstract: The methods of the invention for scanning a band of frequencies using a nuclear quadrupole resonance detection system with an array of high temperature superconductor sensors to detect nuclear quadrupole resonance signals improve the nuclear quadrupole resonance detection system performance.



















†3

†4



WO 2007/064352 A1



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

TITLE

SCANNING A BAND OF FREQUENCIES USING AN ARRAY OF HIGH TEMPERATURE SUPERCONDUCTOR SENSORS TUNED TO THE SAME FREOUENCY

5

This application claims the benefit of U.S. Application No. 11/118,962, filed on April 29, 2005, which is a non-provisional of U.S. Application No. 60/566,953, filed on April 30, 2004, which is incorporated in its entirety as a part hereof for all purposes.

15

10

Field of the Invention

This invention relates to methods and apparatus for scanning a band of frequencies using an array of high temperature superconductor sensors in a nuclear quadrupole resonance detection system.

20

25

30

Background of the Invention

The use of nuclear quadrupole resonance (NQR) as a means of detecting explosives and other contraband has been recognized for some time. See e.g.

T. Hirshfield et al, J. Molec. Struct. 58, 63 (1980),
A.N. Garroway et al, Proc. SPIE 2092, 318 (1993), and
A.N. Garroway et al, IEEE Trans. on Geoscience and
Remote Sensing 39, 1108 (2001). NQR provides some
distinct advantages over other detection methods. NQR
requires no external magnet such as required by nuclear
magnetic resonance. NQR is sensitive to the compounds
of interest, i.e. there is a specificity of the NQR
frequencies.

35

A detection system can have one or more coils that both transmit and receive, or it can have separate coils that only transmit and only receive. A transmit,

or transmit and receive, coil of an NQR detection system provides a radio frequency (RF) magnetic field that excites the quadrupole nuclei in the sample, and results in the production of their characteristic resonance signals that the receive, or transmit and receive, coil (i.e. the sensor) detects. The NQR signals have low intensity and short duration. transmit, receive, or transmit and receive, coil preferably has a high quality factor (Q). The transmit, receive, or transmit and receive, coil has typically been a copper coil and therefore has a Q of about 10². It can be advantageous to use a transmit, receive, or transmit and receive, coil made of a high temperature superconductor (HTS) rather than copper since the HTS self-resonant coil has a Q of the order of $10^4 - 10^6$.

The large Q of the HTS self-resonant coil plays an important role during reception. In view of the low intensity NQR signal, it is important to have a signal-to-noise ratio (S/N) as large as possible. The signal-to-noise ratio is proportional to the square root of Q so that the use of the HTS self-resonant coil results in an increase in S/N by a factor of 10-100 over that of the copper system. The use of a high temperature superconductor sensor, i.e. receive coil, provides a distinct advantage over the use of an ordinary conductor sensor. The HTS sensor can provide greater sensitivity and/or smaller size.

30

35

5

10

15

20

25

The performance of a signal detection system can be improved by using an array of sensors, i.e. receive coils, to scan the band of frequencies of interest as compared to using a single sensor. An object of the present invention is to provide method and apparatus for scanning a band of frequencies using an array of sensors in a nuclear quadrupole resonance detection system.

Summary of the Invention

One embodiment of this invention is a method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein n ≥ 2 and the bandwidth of each sensor is Δf , by

5

10

- (a) determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is of the order of $\Delta F/\Delta f$;
- (b) tuning the resonance frequencies of the n sensors to n different resonance frequencies, wherein the n different resonance frequencies are selected from the group of the r different frequencies, and maintaining these resonance frequencies for a selected period of time;
- (c) retuning simultaneously the resonance frequencies of the n sensors to n different frequencies selected from the group of the r different frequencies, and maintaining these retuned resonance frequencies for a selected period of time, wherein each of the n sensors has a retuned resonance frequency that is different from the resonance frequency to which it was tuned or retuned in any previous step; and
 - (d) repeating step (c) r-2 times wherein the resonance frequency of each sensor is tuned for one period of time to each of the r different frequencies, and no two sensors are tuned to the same resonance frequency at the same time.
- Steps (b), (c) and (d) may be repeated one or more times, the signals detected by all sensors that are tuned to a selected frequency may be combined, and the periods of time for which the resonance frequencies

are maintained in steps (b), (c) and (d) may be the same.

Another embodiment of this invention is a method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein $n \geq 4$ and the bandwidth of each sensor is Δf , by

(a) dividing the sensors into m groups with p sensors in each group, determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is of the order of $\Delta F/\Delta f$, dividing the r different frequencies into s sets with p of the r different frequencies in each set, and assigning each set of frequencies to one of the groups of sensors;

- (b) tuning the resonance frequencies of the p 20 sensors in each group to the p different frequencies in the set of frequencies assigned to that group, and maintaining these tuned resonance frequencies for a selected period of time;
- (c) retuning simultaneously the resonance
 frequencies of the p sensors in each group to p
 different frequencies within the same set assigned to
 that group for step (b), and maintaining these retuned
 resonance frequencies for a selected period of time,
 wherein each of the p sensors has a retuned resonance
 frequency that is different from the resonance
 frequency to which it was tuned or retuned in any
 previous step;
 - (d) repeating step (c) p-2 times;
- (e) retuning the resonance frequencies of the p sensors in each group to the p different frequencies in a second set of frequencies assigned to that group, and maintaining these retuned resonance frequencies for a selected period of time;

(f) retuning simultaneously the resonance frequencies of the p sensors in each group to p different frequencies within the same set assigned to that group for step (e), and maintaining these retuned resonance frequencies for a selected period of time, wherein each of the p sensors has a retuned resonance frequency that is different from the resonance frequency to which it was tuned or retuned in any previous step;

10

5

(g) repeating step (f) p-2 times; and

(h) repeating steps (e), (f) and (g) for each additional set of p different frequencies until all s sets of frequencies have been used as resonance frequencies for one of the m groups of sensors.

15

20

25

30

35

Steps (b) through (h) may be repeated one or more times, the signals detected by all sensors that are tuned to a selected frequency may be combined, and the periods of time for which the resonance frequencies are maintained in steps (b) through (h) may be the same.

A further embodiment of this invention is a method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein $n \geq 4$ and the bandwidth of each sensor is Δf , by

(a) dividing the n sensors into m groups with p sensors in each group, determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is of the order of $\Delta F/\Delta f$, dividing the r different frequencies into m sets with at least p of the r different frequencies in each set, and assigning one set of frequencies to each group of sensors;

(b) tuning the resonance frequencies of the p sensors in each group to p different frequencies selected from any of the frequencies assigned to that group, and maintaining these tuned resonance frequencies for a selected period of time;

5

10

- (c) retuning simultaneously the resonance frequencies of the p sensors in each group to p different frequencies selected from any of frequencies assigned to that group, and maintaining these retuned resonance frequencies for a selected period of time, wherein each of the p sensors has a retuned resonance frequency that is different from the resonance frequency to which it was tuned or retuned in any previous step; and
- (d) repeating step (c) until all of the frequencies in the sets of frequencies assigned to each group have been used as a resonance frequency by each sensor in the group.
- Steps (b), (c) and (d) may be repeated one or more times, the signals detected by all sensors that are tuned to a selected frequency may be combined, and the periods of time for which the resonance frequencies are maintained in steps (b), (c) and (d) may be the same.

Yet another embodiment of this invention is a nuclear quadrupole resonance detection system for scanning a sample, comprising

- 30 (a) n high temperature superconductor sensors, each with bandwidth Δf , to scan a band of frequencies ΔF and detect any nuclear quadrupole resonance signal within the band of frequencies ΔF , wherein $n \geq 2$;
- of the n sensors to n different frequencies, wherein the n different frequencies are selected from the group of r different frequencies that span the band of

frequencies ΔF using sensors with bandwidths Δf , and wherein r is of the order of $\Delta F/\Delta f$; and

(c) means to simultaneously retune r-1 times the resonance frequencies of the n sensors to n different frequencies each time, wherein after each retuning, each of the n sensors has a retuned resonance frequency that is different from any of the resonance frequencies to which it was previously tuned or retuned.

10

15

20

25

30

35

5

Yet another embodiment of this invention is a method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein $n \geq 2$ and the bandwidth of each sensor is Δf , by

- (a) determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is of the order of $\Delta F/\Delta f$;
- (b) tuning the resonance frequencies of the n sensors to n different frequencies, wherein the n different frequencies are selected from the group of the r different frequencies, and maintaining the resonance frequencies of the n sensors for a selected period of time;
- (c) retuning the resonance frequencies of some or all of the n sensors to any of the r different frequencies that were not used in any previous step, wherein the n sensors have n different resonance frequencies, and maintaining the resonance frequencies of the n sensors for a selected period of time; and
- (d) repeating step (c) until all the r different frequencies have been used as resonance frequencies.

Steps (b), (c) and (d) may be repeated one or more times, the signals detected by all sensors that

are tuned to a selected frequency may be combined, the periods of time for which the resonance frequencies are maintained in steps (b), (c) and (d) may be the same, and in step (c) the resonance frequencies of all of the n sensors are retuned to any of the r different frequencies that were not used in any previous step.

5

10

15

20

25

35

Yet another embodiment of this invention is a nuclear quadrupole resonance detection system for scanning a sample, comprising:

- (a) n high temperature superconductor sensors, each with bandwidth Δf , to scan a band of frequencies ΔF and detect any nuclear quadrupole resonance signal within the band of frequencies ΔF , wherein $n \geq 2$;
- (b) means to tune the resonance frequencies of the n sensors to n different frequencies, wherein the n different frequencies are selected from the group of r different frequencies that span the band of frequencies ΔF using sensors with bandwidths Δf , and wherein r is of the order of $\Delta F/\Delta f$; and
- (c) means to simultaneously retune the resonance frequencies of the n sensors to n different frequencies that are not any of the r different frequencies used previously as resonance frequencies, and to continue to retune the n sensors in the same manner until all the r different frequencies have been used as resonance frequencies.
- Yet another embodiment of this invention is a nuclear quadrupole resonance detection system for scanning a sample, comprising:
 - (a) n high temperature superconductor sensors, each with bandwidth Δf , to scan a band of frequencies ΔF and detect any nuclear quadrupole resonance signal within the band of frequencies ΔF , wherein $n \geq 2$; and

(b) means to tune the resonance frequencies of each of the n sensors to r different frequencies, wherein the r different frequencies span the band of frequencies ΔF using sensors with bandwidths Δf and wherein r is of the order of $\Delta F/\Delta f$.

5

10

15

20

25

Yet another embodiment of this invention is a method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein $n \geq 2$ and the bandwidth of each sensor is Δf , by

- (a) determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is the order of $\Delta F/\Delta f$;
- (b) tuning the resonance frequencies of all the n sensors to the same frequency, wherein the frequency is selected from the group of the r different frequencies, and maintaining the resonance frequencies for a selected period of time;
- (c) retuning simultaneously the resonance frequencies of all of the n sensors to the same frequency, wherein the retuned frequency is another of the r different frequencies, and maintaining these retuned resonance frequencies for a selected period of time; and
- (d) repeating step (c) r-2 times, wherein after each retuning the retuned resonance frequencies
 of the n sensors are different from the resonance frequencies to which the sensors are tuned or retuned in any of the previous steps.
- Steps (b), (c) and (d) may be repeated one or more times, the signals detected by all sensors that are tuned to a selected frequency may be combined, and the periods of time for which the resonance frequencies

are maintained in steps (b), (c) and (d) may be the same.

Yet another embodiment of this invention is a nuclear quadrupole resonance detection system for scanning a sample, comprising:

5

10

15

20

25

30

35

- (a) n high temperature superconductor sensors, each with bandwidth Δf , to scan a band of frequencies ΔF and detect any nuclear quadrupole resonance signal within the band of frequencies ΔF , wherein n ≥ 2 ;
- (b) means to tune the resonance frequencies of all the n sensors to the same resonance frequency, wherein the resonance frequency is selected from the group of r different frequencies that span the band of frequencies ΔF using sensors with bandwidths Δf , and wherein r is of the order of $\Delta F/\Delta f$; and
- (c) means to simultaneously retune r-1 times the resonance frequencies of all the n sensors to the same frequency each time, wherein the frequency each time is another of the r different frequencies, and wherein after each retuning each of the n sensors has a retuned resonance frequency that is different from any resonance frequencies to which it has previously been retuned.

The methods of the invention for scanning a band of frequencies in a nuclear quadrupole resonance detection system are especially useful when the nuclear quadrupole resonance detection system is being used for detecting the nuclear quadrupole resonance of explosives, drugs and other contraband.

Brief Description of the Drawings

Figure 1 shows one embodiment for scanning a band of frequencies using an array of four sensors wherein all four sensors have the same resonance

trequency at any given time and are stepped in unison through the frequency band.

Figure 2 shows a second embodiment for scanning a band of frequencies using an array of four sensors wherein the resonance frequencies are initially set at four different frequencies and kept fixed at those frequencies.

5

20

25

30

35

10 Figure 3 shows another embodiment of the invention for scanning a band of frequencies using an array of four sensors wherein the resonance frequencies are initially set at four different frequencies, and the resonance frequencies are then simultaneously retuned to the four different frequencies at 3 subsequent times, wherein each of the four sensors has a retuned resonance frequency that is different from any of its previous resonance frequencies.

Detailed Description of the Preferred Embodiments

This invention provides methods for scanning a band of frequencies in a NQR detection system. This invention also provides NQR detection systems that can accomplish these improved performances.

The high Q and relatively small size of an HTS sensor makes the use of an array of such sensors feasible, and the method of scanning this array is critical to the performance of the NQR detection system using the array. There are various reasons that would make scanning a band of frequencies desirable in a NQR detection system. One motivation for such scanning arises from the temperature dependence of NQR frequencies. The temperature of the sample to be scanned as a source of NQR may be known only within some range of temperature. As a result, the NQR frequency is known only within a range of frequencies, i.e. a band of frequencies. To detect the NQR signal there must be detection capability over the band of

frequencies. Another reason for scanning a band of frequencies is to search for more than one NQR frequency.

One method to carry out such a scan comprises tuning all the sensors in the array to the same frequency, a selected frequency within the band, and then frequency stepping all of the sensors in the array, i.e. changing the resonance frequencies of all the sensors in the array in the same manner. This method is illustrated in Figure 1 with an array of four sensors. For simplicity, four frequency settings f₁, f₂, f₃ and f₄ are assumed to span the frequency band of interest. Figure 1 illustrates the method and shows the resonance frequencies of the four sensors at four different times t₁, t₂, t₃ and t₄. Since the resonance frequencies of the sensors are stepped through the band of frequencies in the same way, all four sensors have the same resonance frequency at any given time.

20

25

30

35

5

10

15

As described above, it is advantageous for sensors to have the high Q of the high temperature superconductor sensors used in this invention. the high Q, there is a corresponding narrow bandpass, i.e. the bandwidth of the sensor $\Delta f = f_R/Q$, where f_R is the resonance frequency. The number of different frequencies r that span the band of frequencies ΔF when using sensors with bandwidths Δf is of the order of $\Delta F/\Delta f$. The ratio $\Delta F/\Delta f = w$, where w is the minimum number of frequencies spanning the band of frequencies ΔF when scanning with sensors of bandwidths Δf , i.e. to span the band of frequencies, the sensors must be tuned to at least w different frequencies. It may be advantageous to increase the number of frequencies used to increase the sensitivity of the measurements. used herein, "the r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is of the order of $\Delta F/\Delta f''$

means that r is at least equal to w, and can be up to three times w.

In view of the narrow bandpass Δf and depending on n, the number of sensors in the array, and the width ΔF of the band of frequencies to be scanned, r may be greater than n. This method of scanning then comprises initially tuning all n sensors to the same frequency where that frequency is selected from the group of r different frequencies. The resonance frequencies of all n sensors are then simultaneously retuned r-1 times, wherein the resonance frequency of all the sensors each time is another of the r different frequencies, and wherein after each retuning the retuned resonance frequencies of the n sensors are different from the resonance frequencies used in any of the previous retunings. Upon completion of the r-1 retunings, all r different frequencies have been used as resonance frequencies. The r different frequencies do not have to be used as resonance frequencies in any particular order. While the sensors will typically be made as essentially identical as possible, there will be some small variation in properties from sensor to sensor, including in Δf .

25

30

35

5

10

15

20

In many NQR detection systems, the sensors will be closely spaced. There is a coupling between these sensors as a result of the mutual inductance between them. This coupling between two sensors increases as the distance between them decreases. The problem of the coupling between sensors is exacerbated when using HTS sensors because of the very large Q's of the HTS sensors. This coupling of sensors can have serious effects on the performance of the NQR detection system. When the sensors are so closely spaced that coupling interferes with detection system performance, it is preferred to employ a device to decouple the sensors. If a device to decouple the sensors is not

employed, however, it would be preferable to use one of the methods of the invention for scanning a band of frequencies described below instead of the method described above in which all the n sensors have the same resonance frequency.

5

One such alternative method to scan a band of frequencies of interest comprises having n sensors in the array with each having a different resonance 10 frequency. The method is illustrated in Figure 2. simplicity and comparison, an array of four sensors and the same four frequencies f_1 , f_2 , f_3 and f_4 used in Figure 1 are used again in Figure 2. The four frequencies are again assumed to span the frequency band of interest. Figure 2 shows the resonance 15 frequencies of the four sensors at four different times t_1 , t_2 , t_3 and t_4 . The resonance frequencies are initially set at four different frequencies and kept fixed at those frequencies. For those situations, in 20 which r is greater than n as discussed above, the resonance frequencies of the n sensors are first tuned to n different frequencies selected from the group of r different frequencies. The resonance frequencies of some or all of the n sensors are then retuned to any of 25 the r different frequencies that were not used previously. Preferably, all of the n sensors are retuned. The retuning is continued until all r frequencies are used as resonance frequencies. Coupling can be further reduced by choosing the n different frequencies, and the sensors with these 30 resonance frequencies, such that, to the extent possible, frequencies are selected that are not too close in frequency and the closer frequencies are spatially separated. While coupling can be reduced by this method, combining the signals from different 35 sensors to achieve noise reduction may have reduced effectiveness, and the spatial sensitivity of the array is limited.

In another embodiment that provides excellent spatial sensitivity and reduced coupling, the method comprises tuning the resonance frequencies of the n 5 high temperature superconductor sensors to n different frequencies, and retuning the resonance frequencies of all of the sensors r-1 times. The resonance frequencies of the n sensors are always different, and the same resonance frequency is used only once for each At the conclusion of the r-1 retunings, all of 1.0 the r different frequencies will have been sued as resonance frequencies for each of the n sensors. method is illustrated in Figure 3 using the same array of four sensors and four frequencies used in Figures 1 Figure 3 shows the resonance frequencies of the 15 four sensors at four different times t_1 , t_2 , t_3 and t_4 . The resonance frequencies of the four sensors are initially set at four different frequencies f1, f2, f3 and f_4 . These four frequencies are assumed to span the frequency band of interest. The resonance frequencies 20 are maintained for a selected period of time and are then simultaneously retuned to the four different frequencies. This simultaneous retuning is repeated two more times with the proviso that each of the four sensors has a retuned resonance frequency that is 25 different from any of its previous resonance frequencies. At the completion of the retunings, each of the sensors has had its resonance frequency set at each of the four frequencies, and each of the frequencies was maintained for the selected period of 30 The four times t_1 , t_2 , t_3 and t_4 represent a time in each of the four given time periods. The four frequencies are shown rotated counter-clockwise among the four sensors in Figure 3, but various assignments of frequencies can be used. 35

When this method is applied in those situations in which r is greater than n as discussed

5

10

15

20

above, the resonance frequencies of the n sensors are first tuned to n different frequencies selected from the group of r different frequencies. The resonance frequencies of the n sensors are then simultaneously retuned to n different frequencies selected from the group of r different frequencies. Each of the n sensors has a retuned resonance frequency that is different from its previously tuned or retuned resonance frequency. The retuning step is repeated r-2 times, wherein each of the n sensors has a retuned resonance frequency that is different from its resonance frequency in any of the previous steps and wherein some or all of the n frequencies selected in any retuning step may be different from the n frequencies selected for the previous tuning. desirable to have those sensors with nearest resonance frequencies spatially separated. This is more readily accomplished as the number of sensors in the array increases. This method of the invention further comprises combining the signals detected by the n sensors when their resonance frequencies were tuned to the same frequency to thereby improve the signal-tonoise ratio.

25 In another embodiment, the method comprises using an array of n high temperature superconductor sensors wherein $n \ge 4$. The method comprises dividing the n sensors into m groups with p sensors in each group, dividing the r different frequencies that span 30 the band of frequencies into s sets with p of the r different frequencies in each set, and assigning each set of frequencies to one of the groups of sensors. the typical situation in which this method would be employed, r would be greater than n so that s would be 35 greater than m, and some or all of the m groups of sensors would be assigned two or more of the s sets of frequencies. The resonance frequencies of the p sensors in each group are tuned to the p different

frequencies in a set assigned to that group. The resonance frequencies of the p sensors in each group are then simultaneously retuned to p different frequencies within the same set previously assigned to that group. Each of the p sensors has a retuned resonance frequency that is different from the resonance frequency to which it was previously tuned or retuned. The retuning step is repeated p-2 times, wherein each of the p sensors in each group has a retuned resonance frequency that is different from the resonance frequency used for it in any of the previous steps.

5

10

The resonance frequencies of the p sensors in 15 each group are then simultaneously retuned to p different frequencies in a second set of frequencies assigned to that group. The resonance frequencies of the p sensors in each group are then simultaneously retuned to p different frequencies in the same second set of frequencies used previously for that group. 20 Each of the p sensors has a retuned resonance frequency that is different from any resonance frequency to which it was previously tuned or retuned. The retuning step is repeated p-2 times, wherein each of the p sensors in each group has a retuned resonance frequency that is 25 different from the resonance frequency used for it in any of the previous steps. Retuning is continued until all s sets of frequencies have been used as resonance frequencies by one of the m groups of sensors. method further comprises combining the signals detected 30 by the p sensors in each group when their resonance frequencies were tuned to the same frequency to thereby improve the signal-to-noise ratio.

Alternatively, the r different frequencies are divided into m sets with at least p of the r different frequencies in each set. One set of frequencies is assigned to each group of sensors. The

resonance trequencies of the p sensors in each group are tuned to p different frequencies selected from any of the frequencies assigned to that group. The resonance frequencies of the p sensors in each group are retuned to p different frequencies selected from any of frequencies assigned to that group. Each of the p sensors has a retuned resonance frequency that is different from the resonance frequency used for it in any previous step. The retuning step is repeated until all of the frequencies in the sets of frequencies assigned to each group have been used as a resonance frequency by each sensor in the group.

5

10

Tuning or retuning the resonance frequency of 15 a sensor may be accomplished in a variety of ways. Means for tuning and/or retuning the resonance frequency of a sensor may include, for example, using two or more movable, coupled high temperature superconductor self-resonant coils. The resonance 20 frequency of the fundamental symmetric mode of the two or more coupled high temperature superconductor selfresonant coils can then be varied by mechanically displacing one or more coils with respect to the others, and these coupled coils as mechanically 25 adjusted will serve as the HTS sensor coil. Preferably, the two or more coils are planar, i.e. surface, coils. Each planar coil can have a HTS coil configuration on only one side of the substrate or essentially identical HTS coil configurations on both 30 sides of the substrate. Preferably, the HTS sensors are each comprised of a high temperature superconductor self-resonant planar coil or two or more coupled high temperature superconductor self-resonant planar coils.

Alternatively, for a sensor comprised of a high temperature superconductor self-resonant coil or two or more coupled high temperature superconductor self-resonant coils, means for tuning and/or retuning

the resonance irrequency of the sensor to a specified frequency may include a circuit, preferably one for each sensor. The circuit is comprised of a single loop or coil to inductively couple the circuit to the high temperature superconductor self-resonant sensor, a 5 reactance in series with the single loop or coil, and means to connect the reactance to, and disconnect the reactance from, the single loop or coil. The single loop or coil can be made of a regular conductor such as 10 copper or a high temperature superconductor. reactance can be an inductance, capacitance or combination of both. Means to connect the reactance to, and disconnect the reactance from, the single loop or coil may include at least one mechanical switch or electrical switch such as a diode. Preferably, the 15 reactance can be varied so that the resonance frequency can be adjusted to more than one frequency. A variable reactance may be provided where the reactance is comprised of two or more capacitors in parallel, each of which can be individually connected to or 20 disconnected from the single loop or coil. Alternatively, a variable reactance may be comprised of two or more inductors in series, each of which can be individually connected to or disconnected from the 25 single loop or coil by a mechanical or electrical switch that can short-circuit the inductor and thereby essentially remove it from the circuit.

quadrupole resonance detection system for scanning a sample. The detection system is comprised of n high temperature superconductor sensors to scan a band of frequencies and detect any nuclear quadrupole resonance signal within the band of frequencies. The detection system also comprises means to tune and/or retune the resonance frequencies of the n sensors to r different frequencies, wherein the r different frequencies span the band of frequencies. As indicated above, means for

tuning and/or retuning may include a circuit comprised of a single loop or coil to inductively couple the circuit to the high temperature superconductor selfresonant sensor, a reactance in series with the single loop or coil, and means to connect the reactance to and disconnect the reactance from the single loop or coil. When two or more coupled high temperature superconductor self-resonant coils are used as a sensor, means for tuning and/or retuning the resonance frequency may include micropositioners to mechanically displace one or more coils with respect to the others. In addition, the detection system is comprised of means to simultaneously retune the resonance frequencies of the n sensors. Means to simultaneously retune the n sensors may include those described above for the initial tuning.

5

10

15

This nuclear quadrupole resonance detection system further comprises means to combine the signals detected by the n sensors when their resonance 20 frequencies were tuned to the same frequency to thereby improve the signal-to-noise ratio. The NQR signals detected by all sensors tuned to a selected resonance frequency can be combined in various ways to enhance detection system performance. For example, means to 25 combine signals may include a programmed microprocessor to add the signals coherently, i.e. the phases of the individual signals are adjusted to add constructively, by various analog and digital techniques. analog technique for coherent addition, the electrical 30 path from each sensor to the combination point, at which the signals are added, is adjusted so that the signals add constructively at the combination point. When the sensors are essentially equidistant from the 35 sample that is the source of the nuclear quadrupole resonance signal, the electrical paths from the sensors to the combination point can be made essentially identical thereby insuring that the signals add

constructively at the combination point. In the digital technique for coherent addition, each signal detected by the sensors is multiplied, before combination, by a constant complex factor that can be measured or calculated to correct for phase differences between the signal paths and thereby insure that the signals add constructively at the combination point. The constant complex factor is specific to each electrical path from each sensor to the combination point. Typically, the signals will be amplified before they are added.

5

10

15

20

35

The advantages of combining signals can be seen as follows. The signal S obtained by coherently adding the signals from n sensors is proportional to n. Assuming that the noise present is random, the noise N, after the coherent addition, is proportional to n^{0.5}. Therefore S/N is proportional to n^{0.5}, i.e. the square root of n. The combination of signals from two sensors therefore increases S/N by a factor of 1.4. The combination of signals from four sensors increases S/N by a factor of 2.

The sensors used to detect the nuclear

quadrupole resonance signals can be used only as
receive coils, or as both transmit and receive coils.

Preferably, separate coils are used to transmit the RF
signal and to detect any NQR signals, and the sensors
are thus used solely as receive coils, i.e. they solely

detect the nuclear quadrupole resonance signals and are
not used to transmit an excitation signal.

The transmit coils used in this invention can be made of normal metals such as copper, silver and aluminum, or can be made from a high temperature superconductor. A normal metal coil is preferably in the form of a shielded-loop resonator (SLR) coil. SLRs have been developed to eliminate the detuning effect of

the electrical interaction between the coil and the surrounding material.

Preferably, one or more SLR copper transmit coils are used to apply an RF signal to the sample to 5 be scanned. Preferably, the sensors are high temperature superconductor (HTS) coils in the form of a self-resonant planar coil, i.e. a surface coil, with a coil configuration of HTS on only one side of the substrate or essentially identical HTS coil 10 configurations on both sides of the substrate. High temperature superconductors are those that superconduct above 77K. The high temperature superconductors used to form the HTS self-resonant coil are preferably selected from the group consisting of YBa2Cu3O7, 15 Tl,Ba,CaCu,O,, TlBa,Ca,Cu,O,, (TlPb)Sr,CaCu,O, and (TlPb) Sr, Ca, Cu, O. Most preferably, the high temperature superconductor is YBa,Cu,O, or Tl,Ba,CaCu,O.

20 An HTS self-resonant coil can be formed by various known techniques. Preferably, a planar coil is formed by first depositing HTS layers on both sides of a single crystal substrate. In a preferred technique for forming a Tl,Ba,CaCu,O, coil, the HTS layers are 25 formed directly on a single crystal LaAlO3 substrate or on a CeO₂ buffer layer on a single crystal sapphire (Al_2O_3) substrate. An amorphous precursor layer of Ba:Ca:Cu oxide about 500 nm thick and with a stoichiometry of about 2:1:2 is deposited by off-axis magnetron sputtering from a Ba:Ca:Cu oxide target. The 30 precursor film is then thallinated by annealing it in air for about 45 minutes at 850°C in the presence of a powder mixture of Tl₂Ba₂Ca₂Cu₃O₁₀ and Tl₂O₃. When this powder mixture is heated, Tl,O evolves from the powder 35 mixture, diffuses to the precursor film and reacts with it to form the Tl, Ba, CaCu, O, phase. The sample is then coated with photoresist on both sides and baked.

A coil design mask is prepared. The design mask is then centered on the photoresist covering the Tl_Ba_CaCu_O film on the front side of the substrate and exposed to ultraviolet light. If the coil is to have the same HTS pattern on both sides of the substrate, the design mask is then centered on the photoresist covering the Tl,Ba,CaCu,O, film on the back side of the substrate and exposed to ultraviolet light. The resist is then developed and the portion of the Tl_Ba_CaCu_O, film exposed when the resist is developed is etched away by argon beam etching. The remaining photoresist layer is then removed by an oxygen plasma. The result is the desired HTS planar coil. If two or more coupled high temperature superconductor selfresonant coils are to be used as the sensor coil, additional coils can be produced using the same technique.

5

10

15

25

30

35

Provision must be made in the detection

20 system of this invention for a power supply to supply power for transmitting an RF excitation pulse.

Provision must also be made for cooling the HTS materials to at least liquid nitrogen temperature.

An NQR detection system comprised of an array of two or more high temperature superconductor sensors can be used to detect the presence of chemical compounds for any purpose, but is particularly useful for detecting the presence of controlled substances such as explosives, drugs or contraband of any kind. Such an NQR detection system could be usefully incorporated into a safety system, a security system, or a law enforcement screening system. Such systems would typically include a mechanical system for automatically moving objects to be scanned into and out of the range of the scanner, and may also include an enclosure in which objects to be subjected to NQR scanning could be placed and shielded from the environment during the

test. where such an enclosure is used, the mechanical system would automatically moving objects to be scanned into and out of the enclosure.

Where an apparatus or method of this invention is stated or described as comprising, including, containing, having, being composed of or being constituted by certain components or steps, it is to be understood, unless the statement or description explicitly provides to the contrary, that one or more components or steps other than those explicitly stated or described may be present in the apparatus or method. In an alternative embodiment, however, the apparatus or method of this invention may be stated or described as consisting essentially of certain components or steps, in which embodiment components or steps that would materially alter the principle of operation or the distinguishing characteristics of the apparatus or method would not be present therein. In a further alternative embodiment, the apparatus or method of this invention may be stated or described as consisting of certain components or steps, in which embodiment components or steps other than those as stated or described would not be present therein.

25

30

5

10

15

20

Where the indefinite article "a" or "an" is used with respect to a statement or description of the presence of a component in an apparatus, or a step in a method, of this invention, it is to be understood, unless the statement or description explicitly provides to the contrary, that the use of such indefinite article does not limit the presence of the component in the apparatus, or of the step in the method, to one in number.

CLAIMS

What is claimed is:

5

10

15

20

25

- 1. A method for scanning a band of frequencies ΔF with a nuclear quadrupole resonance detection system comprising an array of n high temperature superconductor sensors to detect nuclear quadrupole resonance signals, wherein $n \geq 2$ and the bandwidth of each sensor is Δf , comprising:
 - a) determining r different frequencies that span the band of frequencies ΔF when using sensors with bandwidths Δf , wherein r is the order of $\Delta F/\Delta f$;
 - b) tuning the resonance frequencies of all the n sensors to the same frequency, wherein the frequency is selected from the group of the r different frequencies, and maintaining the resonance frequencies for a selected period of time;
 - c) retuning simultaneously the resonance frequencies of all of the n sensors to the same frequency, wherein the retuned frequency is another of the r different frequencies, and maintaining these retuned resonance frequencies for a selected period of time; and
 - d) repeating step (c) r-2 times, wherein after each retuning the retuned resonance frequencies of the n sensors are different from the resonance frequencies to which the sensors are tuned or retuned in any of the previous steps.
- 2. The method of claim 1, further comprising repeating steps (b), (c) and (d) one or more times.

3. The method of claim 1, further comprising combining the signals detected by all sensors that are tuned to a selected frequency.

- 5 4. The method of claim 1, wherein each resonance frequency is maintained for the same period of time.
- 5. The method of claim 1, wherein the n high temperature superconductor sensors solely detect nuclear quadrupole resonance signals.

15

20

25

30

- 6. The method of claim 5, wherein each high temperature superconductor sensor is comprised of a high temperature superconductor self-resonant planar coil.
 - 7. The method of claim 5, wherein each high temperature superconductor sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils.
 - 8. A nuclear quadrupole resonance detection system for scanning a sample, comprising:
 - a) n high temperature superconductor sensors, each with bandwidth Δf , to scan a band of frequencies ΔF and detect any nuclear quadrupole resonance signal within the band of frequencies ΔF , wherein $n \geq 2$;
 - b) means to tune the resonance frequencies of all the n sensors to the same resonance frequency, wherein the resonance frequency is selected from the group of r different frequencies that span the band of frequencies ΔF using sensors with bandwidths Δf , and wherein r is of the order of $\Delta F/\Delta f$; and
 - c) means to simultaneously retune r-1 times the resonance frequencies of all the n sensors to the same frequency each time, wherein the

frequency each time is another of the r different frequencies, and wherein after each retuning each of the n sensors has a retuned resonance frequency that is different from any resonance frequencies to which it has previously been retuned.

9. The nuclear quadrupole resonance detection system of claim 8, further comprising:

- d) means to combine the signals detected by all sensors that are tuned to a selected frequency.
- 10. The nuclear quadrupole resonance detection system of claim 8, wherein the n high temperature superconductor sensors solely detect nuclear quadrupole resonance signals.
- 11. The nuclear quadrupole resonance detection system of claim 10, wherein each high temperature superconductor sensor is comprised of a high temperature superconductor self-resonant planar coil.
- 12. The nuclear quadrupole resonance detection system of claim 10, wherein each high temperature superconductor sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils.
- 13. The nuclear quadrupole resonance detection

 30 system of claim 10, further comprising one or more shielded-loop resonator coils to apply to the sample to be scanned for nuclear quadrupole resonance an RF signal capable of exciting quadrupolar nuclei in the sample.

35

5

10

15

20

25

14. The nuclear quadrupole resonance detection system of claim 10, wherein the means to tune and simultaneously retune the resonance frequency of each

of the n sensors is comprised of n circuits, one for each of the n sensors, wherein each circuit is comprised of (a) a single loop or coil to inductively couple the circuit to the high temperature superconductor self-resonant sensor, (b) a variable reactance in series with the single loop or coil, and

(c) means to connect the variable reactance to, and

disconnect the variable reactance from, the single loop

10

or coil.

5

15. The nuclear quadrupole resonance detection system of claim 10, wherein the means to tune and simultaneously retune the resonance frequency of each of the n sensors is comprised of one or more circuits that is comprised of a variable reactance.

16. The nuclear quadrupole resonance detection system of claim 8, wherein the sample comprises explosives, drugs or other contraband.

20

15

- 17. The nuclear quadrupole resonance detection system of claim 9, wherein the sample comprises explosives, drugs or other contraband.
- 25 18. A safety system, a security system, or a law enforcement screening system comprising the nuclear quadrupole resonance detection system of claim 9.

1/3

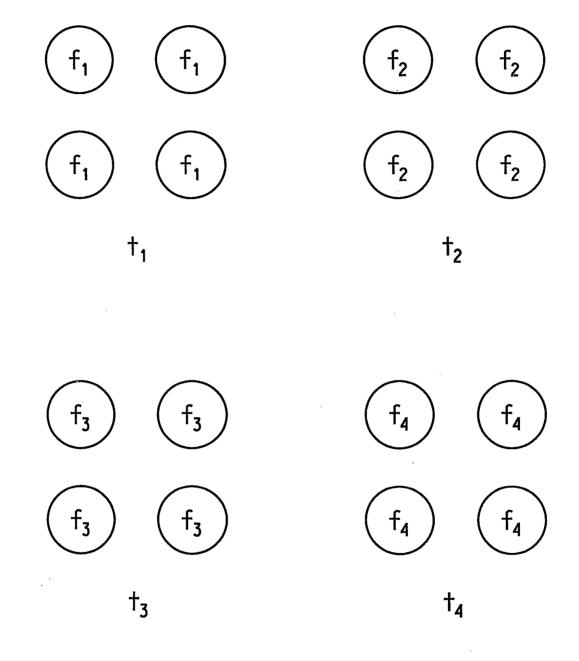


FIG. 1

2/3

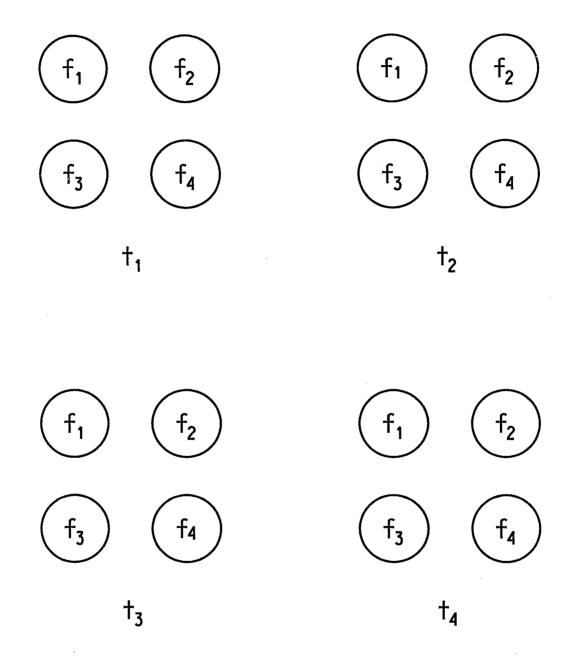


FIG. 2

3/3

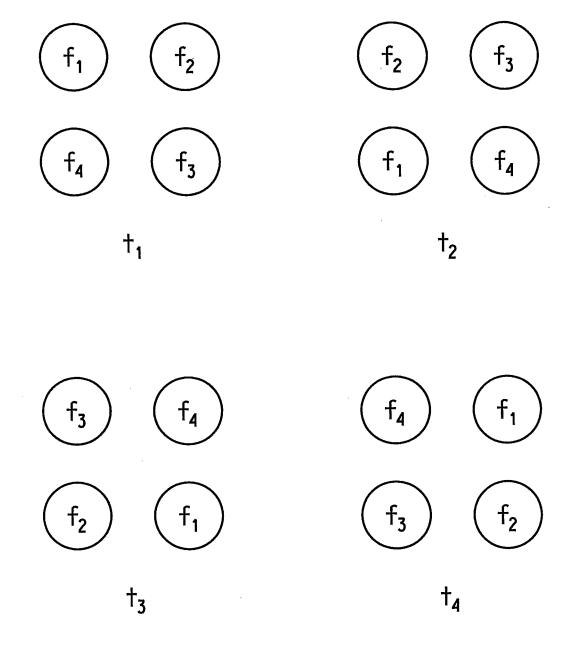


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No PCT/US2006/015460

A. CLASSIFICATION OF SUBJECT MATTER INV. G01R33/3415

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 $\label{lem:minimum documentation searched (classification system followed by classification symbols) \\ GO1R$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the	Relevant to claim No.		
X	WO 99/45409 A (BTG INTERNATION ROWE, MICHAEL, DAVID; SMITH, J SYDNEY) 10 September 1999 (199 page 23, paragraph 3 - page 23 4 abstract page 8, paragraph 5	1–18		
X	WO 03/096041 A (QRSCIENCES TEC PTY LTD; RUDAKOV, TARAS, NIKOL MIKHALT) 20 November 2003 (200 page 19, paragraph 4 abstract	1–18		
X	WO 98/37438 A (ADVANCED IMAGIN INC) 27 August 1998 (1998-08-2 abstract page 16, paragraph 5	1,8,14		
X Furt	ther documents are listed in the continuation of Box C.	_/X See patent family annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filling date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filling date but		cited to understand the principle or the invention "X" document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an indocument is combined with one or ments, such combination being obvio in the art.	 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled 	
	actual completion of the international search	Date of mailing of the international sea	rch report	
	all July 2006 mailing address of the ISA/	04/08/2006 Authorized officer		
	European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dragomir, A		

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/015460

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
		Helevant to claim No.
X	WO 00/70356 A (INTERMAGNETICS GENERAL CORPORATION) 23 November 2000 (2000-11-23) abstract page 5, paragraphs 1,2	1,6-8, 11,12
		,

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2006/015460

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9945409	A	10-09-1999	AU CA EP	3267999 A 2322500 A1 1060404 A1	20-09-1999 10-09-1999 20-12-2000
WO 03096041	Α	20-11-2003	US	2005146331 A1	07-07-2005
WO 9837438	Α	27-08-1998	AU	6182798 A	09-09-1998
WO 0070356	Α	23-11-2000	AU	5441100 A	05-12-2000