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(54) Title: THE USE OF TWO OR MORE SENSORS TO DETECT DIFFERENT NUCLEAR QUADRUPOLE RESONANCE SIGNALS OF A TARGET COMPOUND

(57) Abstract: The use of two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of a target compound to detect the different nuclear quadrupole resonance signals greatly reduces the chance of misidentification, and thereby improves nuclear quadrupole resonance detection system performance.

TITLE
THE USE OF TWO OR MORE SENSORS TO DETECT DIFFERENT NUCLEAR QUADRUPOLE RESONANCE SIGNALS OF A TARGET COMPOUND

This application claims the benefit of U.S. Provisional Application No. 60/541,784, filed February 4, 2004, which is incorporated in its entirety as a part hereof for all purposes.

Field of the Invention

This invention relates to a nuclear quadrupole resonance detection system and to the use therein of two or more sensors. The sensors are tuned to at least two different nuclear quadrupole resonance frequencies of a target compound to detect the different nuclear quadrupole resonance signals, and thereby provide improved nuclear quadrupole resonance detection system performance.

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.

One technique for measuring NQR in a sample is to place the sample within a solenoid coil that surrounds the sample. The coil provides a radio frequency (RF) magnetic field that excites the quadrupole nuclei in the sample and results in their producing their characteristic resonance signals. This is the typical apparatus configuration that might be used for scanning mail, baggage or luggage.

There is also a need for a NQR detector that permits detection of NQR signals from a source outside the detector, *e.g.* a wand detector, that could be passed over persons or containers as is done with existing metal detectors. Problems associated with such detectors using conventional systems are the decrease in detectability with distance from the detector coil, and the associated equipment needed to operate the system.

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 their producing their characteristic resonance signals that the coil receives. The NQR signals have low intensity and short duration. The 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 10^2.

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 10^3-10^6. The large Q of the HTS self-resonant coil produces large magnetic field strengths during the RF transmit pulse and does so at lower RF power levels. This dramatically reduces the amount of transmitted power required to produce NQR signals for detection, and thereby reduces the size of the RF power supply sufficiently so that it can be run on portable batteries.

The large Q of the HTS self-resonant coil also plays an important role during the receive time. 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.

These advantages during both the transmit and the receive times enable a detector configuration that is small and portable. In particular, the use of a high temperature superconductor sensor receive coil prepared from a high temperature superconductor material, provides a distinct advantage over the use of an ordinary conductor coil.

One goal in using NQR for the detection of contraband is to minimize the number of erroneous results. A target compound that is an NQR source has a plurality of signature NQR frequencies, *i.e.* a set of NQR frequencies that is specific to that compound. Any one of these frequencies may overlap the NQR line of another compound. With a sensor tuned to such a frequency there can be false-positive identifications as a result of the intentional or inadvertent presence of the other compound.

An object of the present invention is to provide a NQR detection system with improved performance with respect to misidentification of an NQR source.

Summary of the Invention

One embodiment of this invention is a method of detecting nuclear quadrupole resonance in a target compound by applying a radio frequency magnetic field to the target compound, and providing two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of the target compound to detect the different nuclear quadrupole resonance signals thereof.

Another embodiment of this invention is a method of detecting nuclear quadrupole resonance in a target compound by applying a radio frequency magnetic field to the target compound, and providing N sensors tuned to M different nuclear quadrupole resonance frequencies of the target compound to detect the M different nuclear quadrupole resonance signals thereof, wherein $N \geq 2$ and $2 \leq M \leq N$.

A further embodiment of this invention is a nuclear quadrupole resonance detection system that includes two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of a target compound, wherein the sensors detect the different nuclear quadrupole resonance signals characteristic of the target compound.

Yet another embodiment of this invention is a nuclear quadrupole resonance detection system that includes N sensors tuned to M different nuclear quadrupole resonance frequencies of a target compound, wherein the N sensors detect the M different nuclear quadrupole resonance signals, and wherein $N \geq 2$ and $2 \leq M \leq N$.

Preferably, the two or more sensors are used solely for sensing, *i.e.* receiving, the NQR signals, and one or more separate coils are used as the transmit, *i.e.* excitation, coils to provide the RF magnetic field that excites the quadrupole nuclei in the target compound to be scanned. Preferably, each sensor is a high temperature superconductor coil. More preferably, each sensor is comprised of a high temperature superconductor self-resonant planar coil, or is comprised of two or more coupled high temperature superconductor self-resonant planar coils.

This invention for improving the reliability of the identification of a target compound, and thereby improving the performance of a nuclear quadrupole resonance detection system, is especially important when the nuclear quadrupole resonance detection system is used for detecting the nuclear quadrupole resonance of explosives, drugs and other contraband.

Detailed Description of the Preferred Embodiments

This invention provides a method of nuclear quadrupole detection in which the false alarm rate is improved by requiring confirmation of the presence of at least two different NQR frequencies of a target compound. This invention also provides an NQR detection system that can accomplish this improved performance.

In this invention, two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of a target compound are used to detect the different nuclear quadrupole resonance signals emitted by the compound. That is, this invention uses N sensors, wherein $N \geq 2$. These N sensors are tuned to M different nuclear quadrupole resonance frequencies, wherein $2 \leq M \leq N$. For example, if 3 sensors were used, 2 sensors could be tuned to one nuclear quadrupole resonance frequency, and the other sensor could be tuned to a different nuclear quadrupole resonance frequency of the same compound. Alternatively, the 3 sensors could be tuned to 3 different nuclear quadrupole resonance frequencies of the same compound.

While one of the NQR frequencies of the target compound may overlap an NQR line of another compound, it is unlikely that two or more NQR frequencies of the target compound would both or all overlap NQR lines of the other compound. Therefore, the use of two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of the target compound to detect the different nuclear quadrupole resonance signals, and thereby make an identification of the target compound, greatly reduces the probability of a false-positive identification.

A "sensor" as used in this invention is a receive device, such as a receive coil, and the sensors used to detect nuclear quadrupole resonance in a target compound will typically be used as receive coils only. In certain embodiments, it may be possible to use them as transmit and receive coils, but, preferably, separate coils are used to transmit the RF signal, and the sensors (as their name implies) are used solely as receive coils.

Preferably, the two or more sensors are high temperature superconductor (HTS) coils. A high temperature superconductor coil is preferably in the form of a self-resonant planar coil, *i.e.* a surface coil, with a coil configuration of HTS on one or both sides of a 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 $YBa_2Cu_3O_7$, $Tl_2Ba_2CaCu_2O_8$, $TlBa_2Ca_2Cu_3O_9$,

$(TlPb)Sr_2CaCu_2O_7$ and $(TlPb)Sr_2Ca_2Cu_3O_9$. Most preferably, the high temperature superconductor is $YBa_2Cu_3O_7$ or $Tl_2Ba_2CaCu_2O_8$.

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 $Tl_2Ba_2CaCu_2O_8$ coil, the HTS layers are formed directly on a single crystal $LaAlO_3$ substrate or on a CeO_2 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 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 $Tl_2Ba_2Ca_2Cu_3O_{10}$ and Tl_2O_3. When this powder mixture is heated, Tl_2O evolves from the powder mixture, diffuses to the precursor film and reacts with it to form the $Tl_2Ba_2CaCu_2O_8$ 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 $Tl_2Ba_2CaCu_2O_8$ 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 $Tl_2Ba_2CaCu_2O_8$ film on the back side of the substrate and exposed to ultraviolet light. The resist is then developed on both sides of the substrate and the portion of the $Tl_2Ba_2CaCu_2O_8$ 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 coil. If two coupled high temperature superconductor self-resonant coils are to be used as the sensor coil, a second coil can be produced using the same technique.

HTS self-resonant coils have high Q's and relatively small size. The use of HTS self-resonant coils as sensors makes the use of an array of two or more sensors in the instant invention especially attractive. If one or more HTS coils are used, provision must also be made for cooling the HTS to liquid nitrogen temperature.

It is often advantageous to be able to fine-tune the resonance frequency of the sensor. One means for accomplishing such tuning is to use two or more coupled high temperature superconductor self-resonant coils. The resonance frequency of the fundamental symmetric mode of the two or more coupled high temperature superconductor self-resonant coils can be varied by mechanically displacing the coils with respect to one another, and these coupled coils may serve as the HTS sensor. Preferably, the two or more coils are planar, *i.e.* surface, coils. Each planar coil has a HTS coil configuration on only one side of the substrate, or has essentially identical HTS coil configurations on both sides of the substrate. Most preferably, the HTS sensor coils are each comprised of a high temperature superconductor self-resonant planar coil or two or more coupled high temperature superconductor self-resonant planar coils.

As indicated above, when two or more coupled high temperature superconductor self-resonant coils are used as a sensor, the resonance frequency of the fundamental symmetric mode of the two or more coupled high temperature self-resonant coils can be varied by mechanically displacing one coil with respect to the other. Means for tuning the resonance frequency of the sensor to a specified nuclear quadrupole resonance frequency thus includes actuators to mechanically displace the coils as described above.

Alternatively, for a sensor comprised of a high temperature superconductor self-resonant coil or two coupled high temperature superconductor self-resonant coils, means for tuning the resonance frequency of the sensor to a specified nuclear quadrupole resonance frequency may also include a circuit. The circuit may be comprised of a single loop or coil to inductively couple the circuit to the high temperature superconductor self-resonant sensor, a reactance in series with the single loop or coil, and means to connect and disconnect the reactance to and from the single loop or coil. In essence, the tuning circuit is resonated which causes a mode split by coupling to the self-resonant high temperature superconductor sensor.

The single loop or coil can be made of a regular conductor such as copper or a high temperature superconductor. The reactance can be an inductance, capacitance or combination of both. The means to connect and disconnect the reactance to and from the single loop or coil may include at least one mechanical switch or electrical switch such as a diode. Preferably, the reactance can be varied so that the resonance frequency can be adjusted to more than one frequency. A variable reactance may be provided in the form of two or more capacitors in parallel, each of which can be individually connected to or disconnected from the single loop or coil. Alternatively, a variable reactance may comprise two or more inductors in series, each of which can be individually connected to or disconnected from the single loop or coil by a mechanical or electrical switch that can short-circuit the inductor, and thereby essentially remove it from the circuit.

The transmit coils used in this invention can be made of copper, silver, aluminum or a high temperature superconductor. A copper, silver or aluminum coil is preferably in the form of a shielded-loop resonator (SLR) coil. SLR's 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 the RF signal to the sample.

More than one transmit coil may be needed to apply the RF signal necessary to excite the quadrupole nuclei and produce the various different nuclear quadrupole resonance signals characteristic of the target compound. Provision must be made for a power supply to supply power for transmitting the RF pulse.

While the discussion herein is presented primarily in terms of the use of a coil as the transmit, receive or transmit and receive device, this invention is not limited thereto, and is applicable to transmit, receive and transmit and receive devices that may have a configuration other than that of a coil.

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 would not be present therein.

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:

1. A method of detecting nuclear quadrupole resonance in a target compound comprising applying a radio frequency magnetic field to the target compound, and providing two or more sensors tuned to at least two different nuclear quadrupole resonance frequencies of the target compound to detect the different nuclear quadrupole resonance signals thereof.

2. The method of claim 1, wherein each sensor is a high temperature superconductor self-resonant planar coil, and wherein each sensor solely detects nuclear quadrupole resonance signals.

3. The method of claim 1, wherein each sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils, and wherein each sensor solely detects nuclear quadrupole resonance signals.

4. The method of claim 2 or 3, further comprising providing one or more shielded-loop resonator coils to apply the RF magnetic field to the target compound to produce at least two different nuclear quadrupole resonance signals.

5. The method of claim 5, wherein the high temperature superconductor self-resonant planar coils are $YBa_2Cu_3O_7$ or $Tl_2Ba_2CaCu_2O_8$ self-resonant planar coils, and wherein each shielded-loop resonator coil is a copper shielded-loop resonator coil.

6. A method of detecting nuclear quadrupole resonance in a target compound comprising applying a radio frequency magnetic field to the target compound, and providing N sensors tuned to M different nuclear quadrupole resonance frequencies of the target compound to detect the M different nuclear quadrupole resonance signals thereof, wherein $N \geq 2$ and $2 \leq M \leq N$.

7. The method of claim 6, wherein each sensor is a high temperature superconductor self-resonant planar coil, and wherein each sensor solely detects nuclear quadrupole resonance signals.

8. The method of claim 6, wherein each sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils, and wherein each sensor solely detects nuclear quadrupole resonance signals.

9. The method of claim 7 or 8, further comprising providing one or more shielded-loop resonator coils to apply the RF magnetic field to the target compound to produce at least M nuclear quadrupole resonance signals.

10. The method of claim 9, wherein the high temperature superconductor self-resonant planar coils are $YBa_2Cu_3O_7$ or $Tl_2Ba_2CaCu_2O_8$ self-resonant planar coils, and wherein each shielded-loop resonator coil is a copper shielded-loop resonator coil.

11. The method of Claim 1 or 6 wherein the target compound comprises explosives, drugs or other contraband.

12. A nuclear quadrupole resonance detection system, comprising two or more sensors tuned to at least two different nuclear quadrupole resonance

frequencies of a target compound, wherein the sensors detect the different nuclear quadrupole resonance signals characteristic of the target compound.

13. The detection system of claim 12, wherein each sensor is a high temperature superconductor self-resonant planar coil, and wherein each sensor detects nuclear quadrupole resonance signals.

14. The detection system of claim 12, wherein each sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils, and wherein each sensor solely detects nuclear quadrupole resonance signals.

15. The detection system of claim 13 or 14, further comprising one or more shielded-loop resonator coils to apply a radio frequency magnetic field to the target compound to produce at least two different nuclear quadrupole resonance signals.

16. The detection system of claim 15, wherein the high temperature superconductor self-resonant planar coils are $YBa_2Cu_3O_7$ or $Tl_2Ba_2CaCu_2O_8$ self-resonant planar coils, and wherein each shielded-loop resonator coil is a copper shielded-loop resonator coil.

17. A nuclear quadrupole resonance detection system, comprising N sensors tuned to M different nuclear quadrupole resonance frequencies of a target compound, wherein the N sensors detect the M different nuclear quadrupole resonance signals, and wherein $N \geq 2$ and $2 \leq M \leq N$.

18. The detection system of claim 17, wherein each sensor is a high temperature superconductor self-resonant planar coil, and wherein each sensor solely detects nuclear quadrupole resonance signals.

19. The detection system of claim 17, wherein each sensor is comprised of two or more coupled high temperature superconductor self-resonant planar coils, and wherein each sensor solely detects nuclear quadrupole resonance signals.

20. The detection system of claim 18 or 19, further comprising one or more shielded-loop resonator coils to apply a radio frequency magnetic field to the target compound to produce at least M different nuclear quadrupole resonance signals.

21. The nuclear quadrupole resonance detection system of claim 20, wherein the high temperature superconductor self-resonant planar coils are $YBa_2Cu_3O_7$ or $Tl_2Ba_2CaCu_2O_8$ self-resonant planar coils, and wherein each shielded-loop resonator coil is a copper shielded-loop resonator coil.

22. The detection system of Claim 12 or 17 wherein the target compound comprises explosives, drugs or other contraband.

INTERNATIONAL SEARCH REPORT

I[illegible]national Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01R33/44

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01R

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, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/45409 A (BTG INTERNATIONAL LTD; ROWE, MICHAEL, DAVID; SMITH, JOHN, ALEC, SYDNEY) 10 September 1999 (1999-09-10) sentence 5, paragraph 2 - sentence 11 abstract -----	1-22
A	US 6 291 994 B1 (KIM YONG-WAH ET AL) 18 September 2001 (2001-09-18) abstract page 2, paragraph 3 - page 5, paragraph 1 page 5, paragraph 1 -----	1-22
A	US 6 150 816 A (SRINIVASAN ET AL) 21 November 2000 (2000-11-21) abstract column 1, paragraph 2 ----- -/--	1-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

I[illegible]ational Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00/70356 A (INTERMAGNETICS GENERAL CORPORATION) 23 November 2000 (2000-11-23) abstract -----	1-22

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