(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 October 2011 (27.10.2011)

PCT

(10) International Publication Number
WO 2011/132092 A1

(51) International Patent Classification:
G01R 33/24 (2006.01)

(21) International Application Number:
PCT/IB2011/051144

(22) International Filing Date:
18 March 2011 (18.03.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/326,775 22 April 2010 (22.04.2010) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(54) Title: NUCLEAR MAGNETIC RESONANCE MAGNETOMETER EMPLOYING OPTICALLY INDUCED HYPERPOLARIZATION

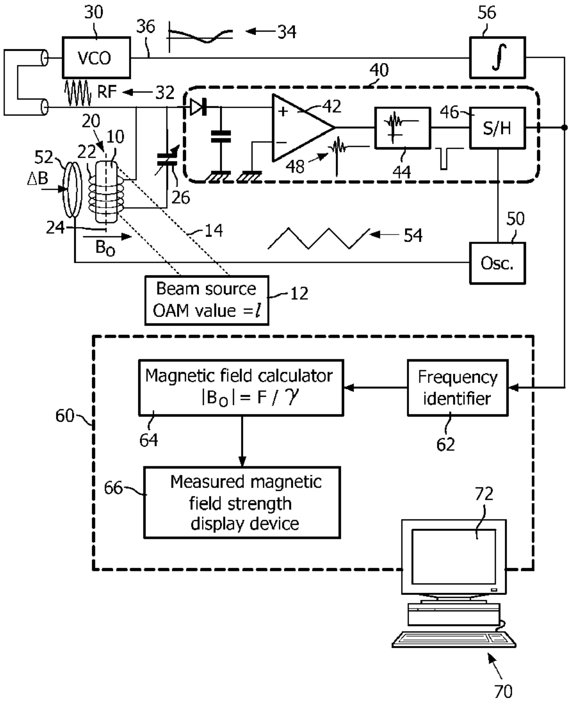

FIG. 1

(57) Abstract: A magnetometer includes: a sample (10) comprising a selected nuclear species; an optical source (12) configured to hyperpolarize the selected nuclear species of the sample by illuminating the sample with optical radiation (14) having orbital angular momentum; a radio frequency generator (20, 26, 30, 150, 152) configured to input radio frequency energy (32) to the hyperpolarized selected nuclear species of the sample over a probed range of radio frequencies; a detector (20, 26, 40, 150, 154, 164, 166) configured to detect a frequency of nuclear magnetic resonance excited in the hyperpolarized selected nuclear species of the sample by the input radio frequency energy; and a signal output generator (64, 66) configured to output a signal indicative of magnetic field strength based on the detected frequency of nuclear magnetic resonance.

WO 2011/132092 A1

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

NUCLEAR MAGNETIC RESONANCE MAGNETOMETER EMPLOYING OPTICALLY INDUCED HYPERPOLARIZATION

DESCRIPTION

The following relates to the magnetic arts, magnetometer arts, magnetic measurement arts, and related arts.

A magnetometer is a device for measuring the strength of a magnetic field. Magnetometers have a diversity of applications, for example in healthcare, industrial, and laboratory applications. Some illustrative magnetometer applications include: magnetic field mapping for magnetic resonance (MR) scanners, synchrotrons, particle accelerators, and other devices employing magnets; detecting underground ores, minerals, unexploded mines, or submarines in the ocean; performing geological and archaeological surveys; performing measurements in a magnetic astronomical observatory; monitoring heart and brain activity; measuring flux distribution inside superconductors; retrieving data stored on magnetic media; directing vehicles on magnetic tracks; providing input to navigation systems; serving as proximity sensors; and counting items on production lines.

Nuclear magnetic resonance (NMR) magnetometers are generally considered to be the "gold standard" for performing field measurements, because NMR is the most accurate field measurement method available. Indeed, NMR magnetometers can achieve accuracies of up to 0.1 ppm. Additionally, NMR provides inherent measurements of the absolute magnetic field strength, whereas other magnetic field measurement techniques typically measure relative field strength and accordingly entail calibration procedures which are prone to errors and can lead to a bias in the measurement.

An NMR magnetometer takes advantage of the fundamental relationship $F=\gamma B$ between the processional frequency (F) of nuclear spins and an applied external magnetic field (B). The parameter γ is the gyrometric ratio, and is a property of a given nuclei species. For example, the gyromagnetic ratio of ^1H hydrogen nuclei is 42.577 MHz/Tesla. In operation, an NMR magnetometer determines the field strength of an unknown magnetic field by placing a small amount of a liquid sample or other sample inside the magnetic field. The sample contains nuclei having a known gyromagnetic ratio. Thus, by measuring the precessional frequency (F) and knowing the gyrometric ratio (γ), the magnetic field strength (B) is determined as $B=F/\gamma$.

A limitation of NMR magnetometers is that they have difficulty measuring weak magnetic fields. As the magnetic field gets weaker, the sample size (and therefore the size of the measurement probe of the NMR magnetometer) becomes larger. A lower limit on sample size is set by signal intensity and signal-to-noise (SNR) requirements, as well as by and practical manufacturing considerations. An upper limit on the measurement probe size is imposed by the desire to have a homogeneous magnetic field within the volume of the probe.

In some NMR magnetometer designs, these limitations of conventional NMR magnetometers are mitigated by "pre-polarizing" the measurement probe sample. Pre-polarizing the sample before using it to measure the strength of a magnetic field enables substantially weaker magnetic fields to be measured, and/or enables the use of substantially smaller probes. Using smaller probes also makes the measurement less sensitive to magnetic field inhomogeneities or gradients, enables measurements to be made in smaller spaces, and enables higher spatial resolution field maps to be measured.

Some pre-polarization methods employ the Overhauser effect. Such "Overhauser magnetometers" take advantage of a phenomenon that affects hydrogen atoms. High frequency radio frequency (RF) power, in the presence of a weak magnetic field, is used to excite unpaired electrons of a small amount of a secondary liquid that is added to the primary liquid sample that contains the hydrogen atoms. This excited electrons cause the hydrogen nuclei in the rest of the liquid to become polarized via the "Overhauser effect" *See, e.g.* Aspinall et al., "Magnetometry for Archaeologists", (Rowman & Littlefield Publishers, Inc, 2008) at pages 47-48. Overhauser magnetometers are energy efficient and have sensitivities suitable for earth field measurement. Power consumption in an Overhauser magnetometer can be optimized to be as low as 1 W for continuous operation, yielding sensitivities between 0.1 nT to 0.01 nT, and sampling rates as high as 5Hz.

The following provides new and improved apparatuses and methods which overcome the above-referenced problems and others.

In accordance with one disclosed aspect, an apparatus comprises a magnetometer that includes: a sample comprising a selected nuclear species; an optical source configured to hyperpolarize the selected nuclear species of the sample by illuminating the sample with optical radiation having orbital angular momentum; a radio frequency generator configured to input radio frequency energy to the hyperpolarized selected nuclear species of the sample over a probed range of radio frequencies; a detector configured to detect a frequency of nuclear magnetic resonance excited in the hyperpolarized selected nuclear species of the sample by the input radio frequency energy; and a signal output generator configured to output a signal indicative of magnetic field strength based on the detected frequency of nuclear magnetic resonance.

In accordance with another disclosed aspect, a method comprises: hyperpolarizing a selected nuclear species of a sample by illuminating the sample with optical radiation having orbital angular momentum; generating nuclear magnetic resonance of the hyperpolarized selected nuclear species of the sample; determining a frequency of the generated nuclear magnetic resonance; and outputting a signal indicative of magnetic field strength based on the determined frequency of the generated nuclear magnetic resonance.

One advantage resides in improved magnetometer sensitivity.

Another advantage resides in providing a magnetometer with a reduced probe size.

Another advantage resides in improved magnetometer spatial resolution.

Further advantages will be apparent to those of ordinary skill in the art upon reading and understanding the following detailed description.

FIGURE 1 diagrammatically illustrates an embodiment of a magnetometer.

FIGURE 2 diagrammatically illustrates selected signals generated by the magnetometer of FIGURE 1.

FIGURE 3 diagrammatically illustrates an embodiment of a light source suitably used in the magnetometer of FIGURE 1 or in the magnetometer of FIGURE 5.

FIGURE 4 diagrammatically illustrates an embodiment of a magnetometer.

FIGURE 5 diagrammatically illustrates selected signals generated by the magnetometer of FIGURE 5.

The nuclear magnetic resonance (NMR) magnetometers disclosed herein employ hyperpolarization of a selected nuclear species by illuminating a sample including the selected nuclear species with optical radiation having orbital angular momentum

(OAM). Light (which, as used herein, encompasses electromagnetic radiation including, for example, visible light, infrared light, or ultraviolet light) having OAM can be generated in various ways, such as by suitable configurations of one or more birefringent plates, polarizers, lenses, phase plates, space light modulators, phase holograms, or so forth. Some suitable approaches for generating light having OAM are disclosed, for example, in: Santamoto, "Photon orbital angular momentum: problems and perspectives", Fortschr. Phys. vol. 52 no. 11-12, pages 1141-53 (2004); Elgort et al., WO 2009/081360 A1; Albu et al., WO 2009/090609 A1; and Albu et al., WO 2009/090610 A1; each of which is incorporated herein by reference in its entirety.

Because angular momentum is a conserved quantity, the OAM of photons absorbed by molecules is transferred in whole to interacting molecules. As a result, affected electron states reach saturated spin states, angular momentum of the molecule about its own center of mass is increased and oriented along the propagation axis of the incident light, and magnetons precession movement of the molecules are also oriented along the propagation axis of the incident light. These effects make it possible to hyperpolarize nuclei within fluids (or, more generally, matter) by illumination with light that carries spin and OAM. In a light beam there is a flow of electromagnetic energy with one component that travels along the vector of the beam propagation, and a second component that rotates about the axis of the beam propagation. The second component is proportional to the angular change of the potential vector around the beam propagation. The rotational energy flow is proportional to a quantiative OAM value, denoted herein as l, and the rotational energy transferred to molecules with which the light interacts is increased with the value of the OAM value l. Since angular momentum is a conserved quantity, when light carrying spin and OAM is absorbed by molecules of matter, the total angular momentum of the system (including both the radiation and the matter) is not changed during absorption and emission of radiation. When a photon is absorbed by an atom, its angular momentum is transferred to the atom. The resulting angular momentum of the atom is then equal to the vector sum of its initial angular momentum plus the angular momentum of the absorbed photon.

Generally, a molecule includes both a nucleus and coupled electrons, and there are both nuclear angular momentum and electron angular momentum types. When a photon interacts with the molecule, the OAM of the electrons is directly coupled to the optical transitions. The different types of angular momentum, however, are coupled to each other by various interactions that allow the polarization to flow from the photon through the electron orbital to nuclear spin, electron spin and molecular rotation reservoirs. *See* Elgort et al., WO 2009/081360 A1; Albu et al., WO 2009/090609 A1; and Albu et al., WO 2009/090610 A1; each of which is incorporated herein by reference in its entirety. The magnitude of the interaction between the photon and the molecule is proportional to the OAM of the photon. Resultantly, the molecular rotation value and orientation changes to tend to align along the direction of propagation of the light, and tend to align molecular nuclei along the same direction. The momenta of molecules are changed in that they are biased toward alignment in a direction along the propagation axis of the incident light by light endowed with spin and OAM proportional to the OAM content of the light.

With reference to FIGURE 1, an illustrative magnetometer employing a continuous wave (CW) measurement approach is diagrammatically illustrated. A sample **10** comprises a selected nuclear species in which NMR is excited to perform a magnetic field strength measurement. The nuclear species may, for example, be an isotope selected from Table 1, which lists some atomic species suitably used as target samples for an NMR magnetometer. Table 1 is not exhaustive, and other nuclear species not listed in Table 1 may also be employed. The choice of the target sample to use in the NMR magnetometer is influenced by the range of magnetic field strengths that are intended to be measured. It is typically advantageous to keep the operational frequency range of an NMR magnetometer within relatively narrow band and at frequencies that are neither too low nor too high. For example, when measuring fields that are between 0.04 to 2T, ^{1}H nuclei are commonly used in the form of water. When measuring magnetic fields between 2T and 14T, ^{2}H nuclei in the form of heavy water containing ^2H_2O molecules are suitable. It is to be understood that the sample **10** includes the target or selected nuclear species, but may optionally also include other atoms, molecules, or substances. For example, in the case of water comprising ^{1}H nuclei, the sample **10** also includes oxygen atoms which are part of the water (H_2O) molecules; similarly, in the case of heavy water comprising ^{2}H nuclei the sample **10** typically also includes both oxygen and a substantial fraction of the hydrogen atoms in the form of ^{1}H nuclei. In some embodiments, the sample **10** may comprise water or another solvent in which a solute that includes the target or selected nuclear species is dissolved. In general, the sample **10** is in liquid form as this phase can provide substantial homogeneity and high molecular packing density; however, the sample **10** may also be a solid, gas, or other phase of matter. As indicated in Table 1, the selection of the target or selected nuclear species determines the gyrometric ratio (γ).

Table 1

Isotope	**gyrometric ratio (γ)**
^{1}H	42.576396 MHz/T
^{2}H	6.535 MHz/T
^{13}C	10.71 MHz/T
^{14}N	3.08 MHz/T
^{19}F	40.08 MHz/T
^{23}Na	11.27 MHz/T
^{27}Al	11.093 MHz/T
^{31}P	17.25 MHz/T

An optical source **12** is configured to hyperpolarize the selected nuclear species of the sample **10** by illuminating the sample **10** with optical radiation **14** having orbital angular momentum (OAM). The optical source **12** can employ any suitable method for imparting to the light beam **14** orbital angular momentum of a selected OAM value (*l*). For example, some suitable approaches for generating light having OAM are disclosed, for example, in: Santamoto, "Photon orbital angular momentum: problems and perspectives", Fortschr. Phys. vol. 52 no. 11-12, pages 1141-53 (2004); Elgort et al., WO 2009/081360 A1; Albu et al., WO 2009/090609 A1; and Albu et al., WO 2009/090610 A1; each of which is incorporated herein by reference in its entirety. An illustative embodiment of the optical source **12** is set forth elsewhere herein with reference to FIGURE 3. The selection of the orbital angular momentum *l*, that is, the OAM value (*l*) is not critical, but in general a larger selected OAM value (*l*) produces a higher degree of hyperpolarization. In some embodiments the optical source **12** is configured to hyperpolarize the selected nuclear species of the sample **10** by illuminating the sample with optical radiation having orbital angular momentum *l* of at least *l*=10, which is effective for producing substantial hyperpolarization so as to enhance magnetometer sensitivity. As mentioned previously, the light **14** having OAM may be visible light, infrared light, ultraviolet light, or so forth. The spectrum of the light **14** can be monochromatic, broadband (e.g., white light), or so forth. The photon energy or energies of the spectrum of the light **14** having OAM should be selected so that the photons are strongly absorbed by the target or selected nuclear species. If the sample **10** includes molecules separate from the target or selected nuclear species (for example, in the case of a solute containing the target or selected nuclear species dissolved in a solvent) then the photon energy or energies of the spectrum of the light **14** having OAM is optionally also selected to provide strong light absorption by the target or selected nuclear species as compared with the molecules that are separate from the target or selected nuclear species (e.g., the solvent).

As diagrammatically indicated in FIGURE 1, a magnetic field B_0 is to be measured by the magnetometer. The magnetic field B_0 has magnitude $|B_0|$ (to be measured) and a direction. In the illustrative example, the magnetic field B_0 has a horizontal direction as diagrammatically depicted in FIGURE 1. The illustrative vector representing B_0 is shown in FIGURE 1 outside of the sample **10** for illustrative convenience – however, it is to be understood that the magnetometer measures the magnitude $|B_0|$ of the magnetic field B_0 within the volume of the sample **10**. If the magnetic field to be measured is spatially inhomogeneous, it is advantageous for the sample **10** to have a small volume so that the magnetometer measures the magnetic field strength at what is approximately a "point" in space. Toward this end, the volume of the sample **10** is optionally small. For example, in some embodiments the sample **10** has a volume of about 100 cubic microns or less. As another example, in some embodiments the sample **10** has a volume of about 10 cubic microns or less. These small sample volumes are enabled because the hyperpolarization of the selected nuclear species provided by the illumination **14** having OAM substantially enhances the sensitivity of the magnetometer. In general, there is a tradeoff between sensitivity and the volume of the sample **10** – thus, in other embodiments the sample **10** may be made substantially larger than 10 cubic microns, or even larger than 100 cubic microns, in order to provide sensitivity effective for measuring low magnetic field strength.

With continuing reference to FIGURE 1, in the illustrative CW measurement configuration the sample **10** is made part of a resonant electrical circuit. For example, the resonant electrical circuit can include: (i) an inductor **20** having a coil **22** and the sample **10** as a core of the coil **22** (illustrated embodiment); or (ii) a capacitor having conductive plates and the sample as a dielectric spacer (embodiment not illustrated); or so forth. In the latter illustrative embodiment employing a capacitor, one or both conductive plates is suitably a grid or other "open" configuration to enable optical illumination of the sample by the optical source **12**. In the illustrated embodiment of the inductor **20**, the windings of the coil **22** are similarly "open", or alternatively the optical source can illuminate the sample along the direction of the coil axis **24** of the coil **22** so that the windings do not block the light having OAM. The illustrative resonant circuit is a series resonant LC circuit including the inductor **20** and a capacitor **26** that can be trimmed to tune the center frequency of the resonant LC circuit. Other resonant circuit configurations besides the illustrative resonant series LC circuit are also contemplated.

The resonant circuit **20**, **26** is a component of a radio frequency generator configured to input radio frequency energy to the hyperpolarized selected nuclear species of the sample over a probed range of radio frequencies. The radio frequency generator includes the resonant circuit **20**, **26** and a voltage controlled oscillator (VCO) **30** that drives the resonant circuit **20**, **26** with input radio frequency energy **32** (diagrammatically indicated in FIGURE 1) whose radio frequency is controlled by an input voltage **34** (diagrammatically indicated in FIGURE 1) supplied at an input **36** of the VCO **30**. The frequency of the input radio frequency energy **32** is swept over the probed range of radio frequencies, where the probed range of radio frequencies is chosen to encompass the range of frequencies $F=\gamma|B_0|$ corresponding to the expected range of magnetic field strengths $|B_0|$ for the magnetic field B_0 to be measured by the magnetometer.

The resonant circuit **20**, **26** is also part of a detector including the resonant circuit **20**, **26** and a readout sub-circuit **40** that in the illustrated embodiment is based on an operational amplifier (op-amp) **42** and also includes a threshold detector **44** and a sample-and-hold (S/H) element **46**. The detector is configured to detect a frequency of NMR excited in the hyperpolarized selected nuclear species of the sample **10** by the input radio frequency energy **32** based on correlation of a resonance of the resonant electrical circuit **20**, **26** with a sweep of input radio frequency energy **32** over the probed range of radio frequencies. When the frequency of the input radio frequency energy **32** equals the NMR frequency ($F=\gamma|B_0|$) for the selected nuclear species in the magnetic field B_0 to be measured, the resonant LC circuit **20**, **26** absorbs part of the input radio frequency energy **32** which results in a decrease in the transmission of the input radio frequency energy **32** to the readout sub-circuit **40**. This results in the diagrammatically illustrated NMR signal **48** having a sharp signal decrease at the time when the frequency of the frequency-swept input radio frequency energy **32** matches the NMR frequency. This sharp signal decrease is detected by the threshold detector **44** and sampled by the S/H element **46**.

In some embodiments, the radio frequency generator comprising the resonant LC circuit **20**, **26** and VCO **30** is driven in an open-loop fashion by the input voltage **34** (diagrammatically indicated in FIGURE 1) supplied at the input **36** of the VCO **30**, with the input voltage **34** being a sinusoidal, triangular, or other time-varying voltage, and the detector comprising the resonant LC circuit **20**, **26** and readout sub-circuit **40** generates the output via the S/H circuit **46** from which the NMR frequency can be determined by correlation with the VCO frequency.

With continuing reference to FIGURE 1 and with further reference to FIGURE 2, in the illustrative embodiment, however, the radio frequency generator and the detector are interconnected in a CW Q-meter configuration such that the frequency of the input radio frequency energy **32** is latched to the NMR frequency and tracks the NMR frequency if it changes with time due to changes in the magnetic field strength $|B_0|$. Toward this end, an oscillator **50** is operatively connected with a radio frequency coil or antenna **52** arranged respective to (e.g., proximate to) the sample **10** to deliver a modulation magnetic field ΔB oriented parallel (or anti-parallel) with the magnetic field B_0 to be measured, as diagrammatically shown in FIGURE 1. Thus, the modulation magnetic field ΔB adds (in a vector sense) to the magnetic field B_0 whose stength $|B_0|$ is to be measured, and the total magnetic field experienced by the sample **10** at any given instant in time is $B_0+\Delta B$. The modulation magnetic field ΔB is modulated using a diagrammatically indicated symmetric triangle-wave modulation **54**. The modulation magnetic field ΔB together with feedback control of the VCO **30** via a feedback loop sub-circuit **56** (which employs integral feedback control, in the diagrammatic embodiment) provides the Q-meter configuration in which the frequency of the input radio frequency energy **32** is latched to and tracks the NMR frequency and tracks the NMR frequency. As diagrammatically shown in FIGURE 2, the resonance peaks of the NMR signal **48** detected during the field modulation **54** generate an error voltage proportional to the distance of the peaks from the zero-crossing of the field modulation **54**. This error voltage is used in the Q-meter configuration of FIGURE 1 to generate a negative feed-back signal that serves as the input voltage **34** supplied at the input **36** of the VCO **30**. The Q-meter configuration described herein with reference to

FIGURES 1 and 2 is further described in Bottura et al., "Field Measurements", Proceedings of the CERN Accelerator School (CAS) on Superconductivity, page 18 (2002), which is incorporated herein by reference in its entirety.

The radio frequency generator and the detector shown in FIGURE 1 are illustrative examples. More generally, any generator/detector circuit configuration can be employed which functions to (i) input radio frequency energy to the hyperpolarized selected nuclear species of the sample and sweep the frequency of the input radio frequency energy over a range of radio frequencies encompassing the expected NMR frequency and (ii) detect the NMR frequency.

With continuing reference to FIGURE 1, a magnetic field readout device **60** is configured to output a signal indicative of magnetic field strength based on the detected NMR frequency. Toward this end, a frequency identifier **62** generates a quantitative representation of the NMR frequency detected by the detector comprising the resonant circuit **20**, **26** and readout sub-circuit **40**. A magnetic field calculator **64** determines the magnetic field strength $|B_0|$ based on the relationship $|B_0|=F/\gamma$ where F is the detected NMR frequency and γ is the gyrometric ratio for the target or selected nuclei of the sample **10**. A display device **66** shows the magnetic field strength in a human perceptible representation, such as by displaying the measured magnetic field strength $|B_0|$ as a numerical value with units of magnetic field, or by displaying a bar whose length is proportional to the measured magnetic field strength $|B_0|$, or so forth.

The magnetic field readout device **60** can be embodied in various ways. In the illustrative embodiment of FIGURE 1, the magnetic field readout device **60** is embodied by a computer **70** having a digital processor (not shown) programmed by suitable software to implement the computation components **62**, **64** and computational aspects fo the display device **66**, and a computer screen **72** for displaying the human-perceptible representation of the measured magnetic field strength $|B_0|$. In other embodiments, the magnetic field readout device **60** may be otherwise embodied, for example as a handheld magnetometer control unit including a digital processor and a dedicated LCD display or other dedicated display. Optionally, the computer **70** or the handheld magnetometer control unit may also include a printed circuit card or other electronic component that embodies other portions of the magnetometer, such as the VCO **30**, the readout sub-circuit **40** of the detector, the oscillator **50**, or so forth.

The magnetic field probe including at least the sample **10** and coil **22** making up the inductor **20** and the beam source **12** arranged to illuminate the sample **10**, and optionally further including the radio frequency coil or antenna **52** providing the optional ΔB modulation, and/or the capacitor **26** or other resonant circuit component or components, and optionally further including various components of the radio frequency generator and/or detector, is suitably configured for insertion into the magnetic field B_0 to be measured, and hence may be, for example, at the tip of a wand, or designed for insertion in a bore of a magnetic resonance scanner, or so forth.

Performance of the magnetometer depends upon orientation of the probe respective to the direction of the magnetic field B_0 to be measured. In some embodiments the probe is handheld or can otherwise be moved to be oriented respective to the magnetic field B_0 in order to obtain the best magnetometer signal. In other embodiments, an array of samples each comprising an instance of the inductor **20** form an array with different orientations, for example arranged in a planar hemispherical configuration or in a three-dimensional half-sphere configuration, and the magnetometer includes further circuitry (not shown) to select the array element providing the best magnetometer signal.

With reference to FIGURE 3, an illustrative example of the beam source **12** is shown. A light source **80** produces light (for example, monochromatic, polychromatic, or broad spectrum visible light, ultraviolet light, infrared light, or so forth, selected to be absorbed by the selected nuclear species of the sample **10**) that is input to a beam expander **82**. In some embodiments, the light source **80** is a white light source. The beam expander **82** includes an entrance collimator **84** for collimating the emitted light into a narrow beam, a concave or dispersing lens **86**, a refocusing lens **88**, and an exit collimator **90** through which the least dispersed frequencies of light are emitted. Other configurations are contemplated for the beam expander **82**. After the beam expander **82**, the light beam is circularly polarized by the combination of a linear polarizer **94** followed by a quarter wave plate **96**. Using circularly polarized light is optional. Other optical preparation operations besides the illustrated beam expansion and circular polarization are contemplated, such as beam collimation, wavelength-selective filtering, intensity modulation, or so forth.

The circularly polarized light is passed through a phase hologram **100** or other component configured to impart orbital angular momentum (OAM) to the light. Some suitable embodiments of the phase hologram **100** are disclosed, for example, in

Elgort et al., WO 2009/081360 A1; Albu et al., WO 2009/090609 A1; and Albu et al., WO 2009/090610 A1; each of which is incorporated herein by reference in its entirety. The phase hologram **100** imparts OAM and spin to an incident beam. In some embodiments, the phase hologram **100** imparts an OAM value l of at least l=10 to the beam. In some embodiments, the phase hologram **100** imparts an OAM value of about l=40 or higher to the light beam. In some embodiments, the phase hologram **100** is a computer generated element that is physically embodied as a spatial light modulator, such as a liquid crystal on silicon (LCoS) panel. In one suitable LcoS panel embodiment of the phase hologram **100**, the panel has 1280×720 pixels, of area 20×20 μm^2, with a 1 μm cell gap. In other embodiments, the phase hologram **100** is embodied by other optics, such as combinations of cylindrical lenses or wave plates. If a spatial light modulator embodiment is employed, then the imparted OAM is optionally software-configurable under control of the computer **70** or another suitably programmed digital processor.

In some embodiments, not all of the light that passes through the holographic plate **100** is imparted with OAM and spin. For example, some OAM-imparting holographic plates have the effect of diffracting the light into different diffraction spot or regions, for example in an Airy pattern. For diffraction by the holographic plate **100** into an Airy pattern, the 0^{th} order diffraction does not have any imparted OAM and the different higher order diffraction spots have different OAM values l, with the maximum probability of OAM interaction being obtained for a light beam with a radius close to the Airy disk radius, and the total OAM in all diffraction spots or regions summing to zero in compliance with conservation of momentum. Accordingly, in the illustrative embodiment of FIGURE 3 a spatial filter or beam stop **104** is placed after the holographic plate **100** to block all diffraction spots or regions except for those carrying light of a desired OAM value l. The selected diffracted beam or beams carrying the desired OAM value l are collected and collimated or focused onto the sample **10** as diagrammatically illustrated illumination **14** by concave mirrors **106**, **108** and a microscope objective lens **110**, as illustrated, or by another optical configuration.

Optionally, optical fibers (not illustrated) may be included in one or more portions of the optical train of the light source **12**, or to convey the light beam **14** to the sample **10**, in order to provide flexibility in the design of the light source **12** and or to provide flexibility in the relative positioning of the light source **12** and the sample **10**. Various other optical configuration variations are also contemplated.

The embodiment of FIGURE 1 is a continuous wave (CW) NMR magnetometer employing hyperpolarization of the target or selected nuclear species of the sample **10** in which the hyperpolarization is achieved using a light beam having orbital angular momentum (OAM). Other NMR magnetometer configurations employing hyperpolarization is achieved using a light beam having OAM are also contemplated.

With reference to FIGURES 4 and 5, another illustrative NMR magnetometer employing hyperpolarization achieved by light having OAM is shown. The NMR magnetometer diagrammatically shown in FIGURE 4 employs a pulsed NMR mode. In the pulsed approach, instead of sending a continuous RF signal that scans a range of frequencies, the pulsed NMR magnetometer uses single broadband radio freuqency pulse to rotate the nuclear magnetic moment of the selected nuclear species of the sample **10** (which is aligned along the magnetic field B_0 to be measured at equilibrium) out of alignment with B_0. The nuclei then precess around B_0 at the precessional frequency until equilibrium conditions return, in a process called a free induction decay (FID). With reference to FIGURE 4, the sample **10** is shown in electromagnetic coupling with a radio frequency coil or antenna **150** that is selectively coupled with either a broadband radio frequency transmitter **152** or with a broadband radio frequency receiver **154** via radio frequency switching circuitry **156**. A magnetometer controller **160** controls the beam source **12** to generate the illumination **14** with OAM.

During an NMR excitation phase the controller **160** causes the receiver **154** to detune from the resonance frequency (if needed to avoid overloading the receiver during the transmit phase), causes the switching circuitry **156** to operatively connect the transmitter **152** with the antenna or coil **150**, and causes the transmitter **152** to input radio frequency energy to the hyperpolarized selected nuclear species of the sample **10** over a broadband encompassing the range of radio frequencies to be probed, that is, encompassing the range of frequencies $F=|B_0|/\gamma$ corresponding to the range of magnetic field strengths $|B_0|$ intended to be within the measurement range of the magnetometer.

After the excitation, the magnetometer controller **160** performs a readout phase by causing the switching circuitry **156** to operatively disconnect the transmitter **152** from the antenna or coil **150** and to operatively connect the receiver **154** to the antenna or coil **150**, and causing the broadband radio frequency receiver **154** to acquire the free induction decay (FID) signal. With brief reference to FIGURE 5, a representative FID signal $\mathbf{S_{FID}}$ is diagrammatically shown. The FID signal is processed by a fast Fourier transform (FFT) processor **164** to generate a FFT spectrum of the FID signal. With brief reference again to FIGURE 5, a representative FFT spectrum $\mathbf{FFT_{FID}}$ is diagrammatically shown, which shows the expected result of a single strong FFT peak corresponding to the NMR frequency of the selected nuclear species of the sample **10** at the magnetic field strength $|B_0|$ of the magnetic field in the sample **10**. A frequency peak detector **166** detects the FFT peak and hence detects the NMR frequency. Optionally, the FFT processor **164** can be replaced by a discrete Fourier transform (DFT) processor or another type of spectral analyzer. It is also noted that commercially available FFT processors sometimes include a built-in peak detector, in which case such an FFT processor can embody both the FFT processor and peak detector components **164**, **166**.

With continuing reference to FIGURE 4, once the NMR frequency is determined the processing is the same as that shown in FIGURE 1. The magnetic field calculator **64** determines the magnetic field strength $|B_0|$ based on the relationship $|B_0|=F/\gamma$ where F is the detected NMR frequency and γ is the gyrometric ratio for the target or selected nuclei of the sample **10**. The display device **66** shows the magnetic field strength in a human perceptible representation, such as by displaying the measured magnetic field strength $|B_0|$ as a numerical value with units of magnetic field, or by displaying a bar whose length is proportional to the measured magnetic field strength $|B_0|$, or so forth.

In the embodiment of FIGURE 4, the antenna or coil **150** is used for both transmit and receive phases, as enabled by the switching circuitry **156**. In an alternative embodiment (not shown), separate transmit and receive coils or antennae can be provided, in which case the switching circuitry is omitted.

The illustrated magnetometers of FIGURES 1 and 4 provide an output in the form of a display of the measured magnetic field strength. More generally, the magnetometer can include a signal output generator configured to output a signal indicative of magnetic field strength based on the detected frequency of nuclear magnetic resonance. For example, in some embodiments the signal output generator is a digital output that sends a digital value indicative of magnetic field strength to another device, such as a monitoring device, without actually displaying the digital value. As another example, in some embodiments the signal output generator is a digital output that stores a digital value indicative of magnetic field strength, again without actually displaying the digital value. In other embodiments, the signal indicative of magnetic field strength may be displayed and stored, or may be displayed and sent to another device, or may be displayed, stored, and sent to another device.

This application has described one or more preferred embodiments. Modifications and alterations may occur to others upon reading and understanding the preceding detailed description. It is intended that the application be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

CLAIMS

Having thus described the preferred embodiments, the invention is now claimed to be:

1. An apparatus comprising:

a magnetometer including:

a sample (10) comprising a selected nuclear species,

an optical source (12) configured to hyperpolarize the selected nuclear species of the sample by illuminating the sample with optical radiation (14) having orbital angular momentum,

a radio frequency generator (20, 26, 30, 150, 152) configured to input radio frequency energy (32) to the hyperpolarized selected nuclear species of the sample over a probed range of radio frequencies,

a detector (20, 26, 40, 150, 154, 164, 166) configured to detect a frequency of nuclear magnetic resonance excited in the hyperpolarized selected nuclear species of the sample by the input radio frequency energy, and

a signal output generator (64, 66) configured to output a signal indicative of magnetic field strength based on the detected frequency of nuclear magnetic resonance.

2. The apparatus as set forth in claim **1**, wherein:

the radio frequency generator (20, 26, 30) is configured to sweep the input radio frequency energy (32) over the probed range of radio frequencies; and

the detector (20, 26, 40) comprises a resonant electrical circuit (20, 26) including at least one of (i) an inductor (20) having the sample (10) as a core of the inductor and (ii) a capacitor having the sample as a dielectric spacer, the detector configured to detect the frequency of nuclear magnetic resonance based on a signal generated by the resonant electrical circuit.

3. The apparatus as set forth in claim **1**, wherein:

the radio frequency generator (150, 152) is configured to input broadband radio frequency energy to the hyperpolarized selected nuclear species of the sample (10) wherein the broadband radio frequency energy encompasses the probed range of radio frequencies; and

the detector (150, 154, 164, 166) comprises a radio frequency coil (150) configured to detect nuclear magnetic resonance emanating from the sample and a spectrum analyzer (164, 166) configured to determine the frequency of the nuclear magnetic resonance detected by the radio frequency coil.

4. The apparatus as set forth in any one of claims **1-3**, wherein the optical source (12) is configured to hyperpolarize the selected nuclear species of the sample (10) by illuminating the sample with optical radiation having orbital angular momentum and circular polarization.

5. The apparatus as set forth in any one of claims **1-4**, wherein the optical source (12) is configured to hyperpolarize the selected nuclear species of the sample (10) by illuminating the sample with optical radiation having orbital angular momentum l of at least $l=10$.

6. The apparatus as set forth in any one of claims **1-5**, wherein the sample (10) comprises water and the selected nuclear species comprise ^1H nuclei.

7. The apparatus as set forth in any one of claims **1-5**, wherein the sample (10) comprises heavy water containing ^2H_2O molecules and the selected nuclear species comprise ^2H nuclei.

8. The apparatus as set forth in any one of claims **1-5**, wherein the selected nuclear species is selected from a group consisting of the isotopes ^1H, ^2H, ^{13}C, ^{14}N, ^{19}F, ^{23}Na, ^{27}Al, and ^{31}P.

9. The apparatus as set forth in any one of claims **1-8**, wherein the signal output generator (64, 66) comprises:

a display device (66, 72) showing the magnetic field strength.

10. The apparatus as set forth in any one of claims **1-9**, wherein the sample (10) has a volume of about 100 cubic microns or less.

11. The apparatus as set forth in any one of claims **1-9**, wherein the sample (10) has a volume of about 10 cubic microns or less.

12. A method comprising:

hyperpolarizing a selected nuclear species of a sample (10) by illuminating the sample with optical radiation (14) having orbital angular momentum;

generating nuclear magnetic resonance of the hyperpolarized selected nuclear species of the sample;

determining a frequency of the generated nuclear magnetic resonance; and

outputting a signal indicative of magnetic field strength based on the determined frequency of the generated nuclear magnetic resonance.

13. The method as set forth in claim **12**, wherein the generating comprises inputting radio frequency energy to the sample (10) including sweeping the input radio frequency energy over a probed range of radio frequencies.

14. The method as set forth in claim **12**, wherein the generating comprises inputting broadband radio frequency energy to the sample wherein the broadband radio frequency energy encompasses a probed range of radio frequencies.

15. The method as set forth in any one of claims **12-14**, wherein the hyperpolarizing comprises:

hyperpolarizing the selected nuclear species of the sample (10) by illuminating the sample with optical radiation having orbital angular momentum l of at least l=10.

16. The method as set forth in any one of claims **12-15**, wherein the selected nuclear species comprise ^1H nuclei.

17. The method as set forth in any one of claims **12-15** wherein the selected nuclear species comprise ^{2}H nuclei.

18. The method as set forth in any one of claims **12-15**, wherein the selected nuclear species is selected from a group consisting of the isotopes ^{1}H, ^{2}H, ^{13}C, ^{14}N, ^{19}F, ^{23}Na, ^{27}Al, and ^{31}P.

19. The method as set forth in any one of claims **12-18**, wherein the outputting comprises:

displaying the magnetic field strength as a numerical value with units of magnetic field on a display device (66, 72).

20. The method as set forth in any one of claims **12-18**, wherein the outputting comprises:

displaying the magnetic field strength on a display device (66, 72).

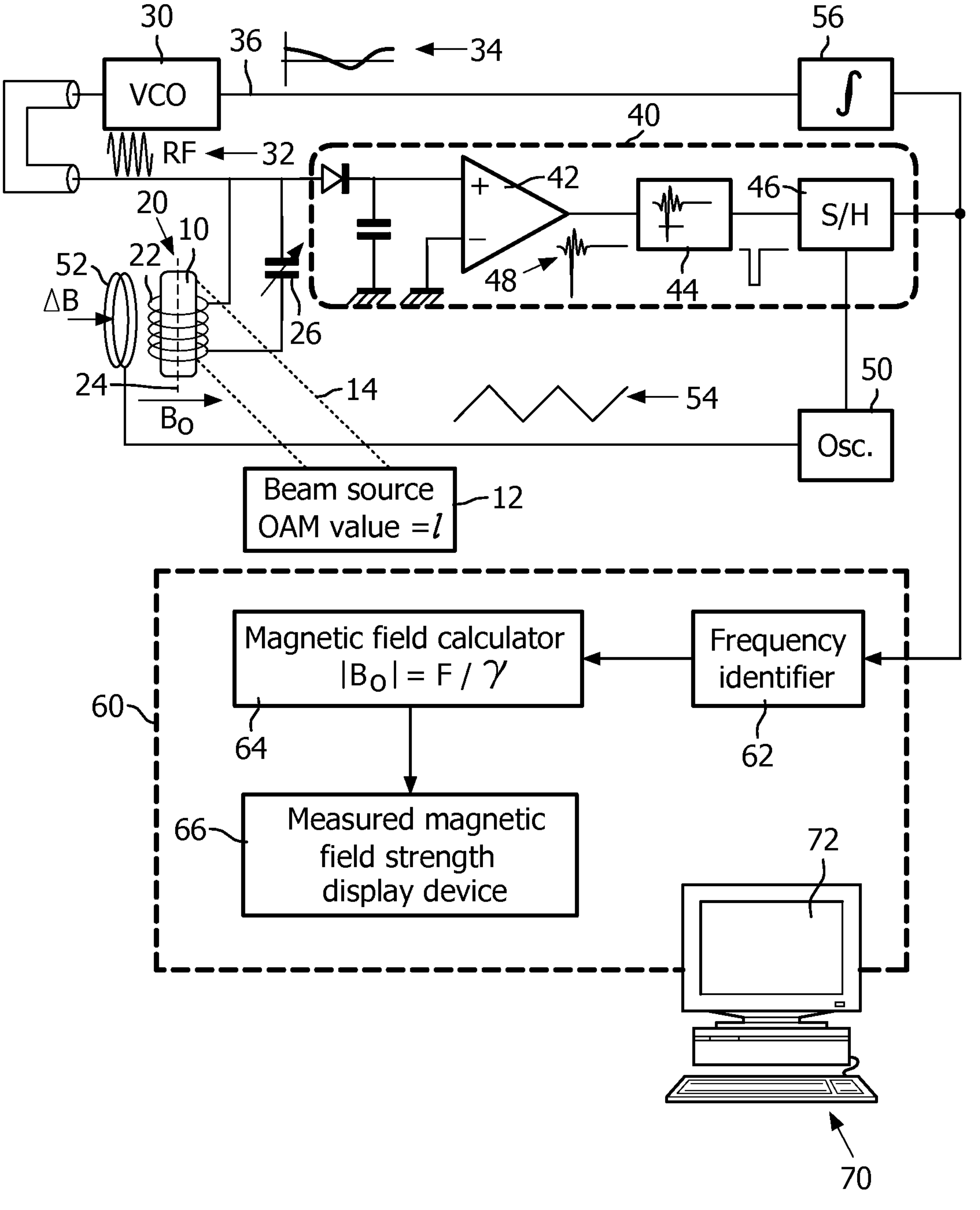
30
VCO
36
34
56
∫
40
RF
32
42
+
−
46
S/H
20
10
22
52
ΔB
26
48
44
24
14
54
50
B_O
Osc.
Beam source
OAM value = l
12
Magnetic field calculator
$|B_O| = F / \gamma$
Frequency identifier
60
64
62
66
Measured magnetic field strength display device
72
70

FIG. 1

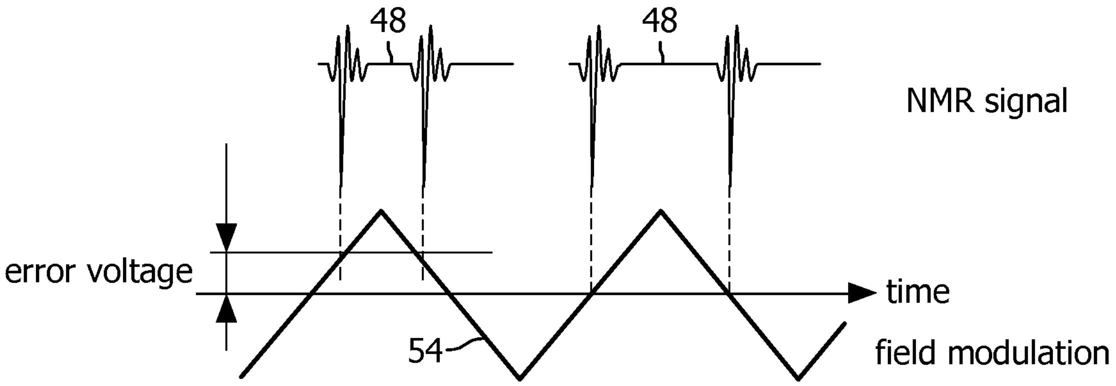

FIG. 2

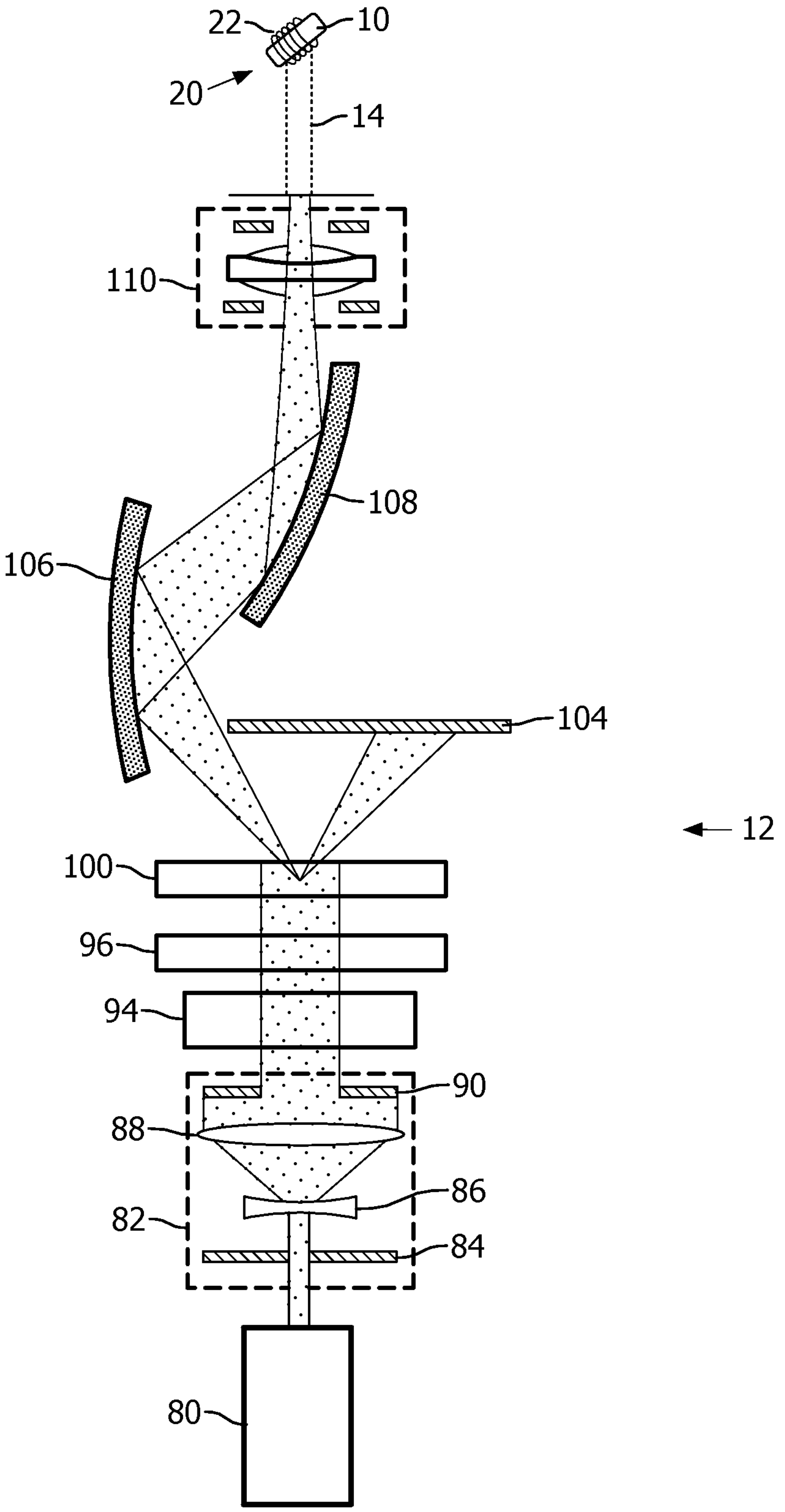

FIG. 3

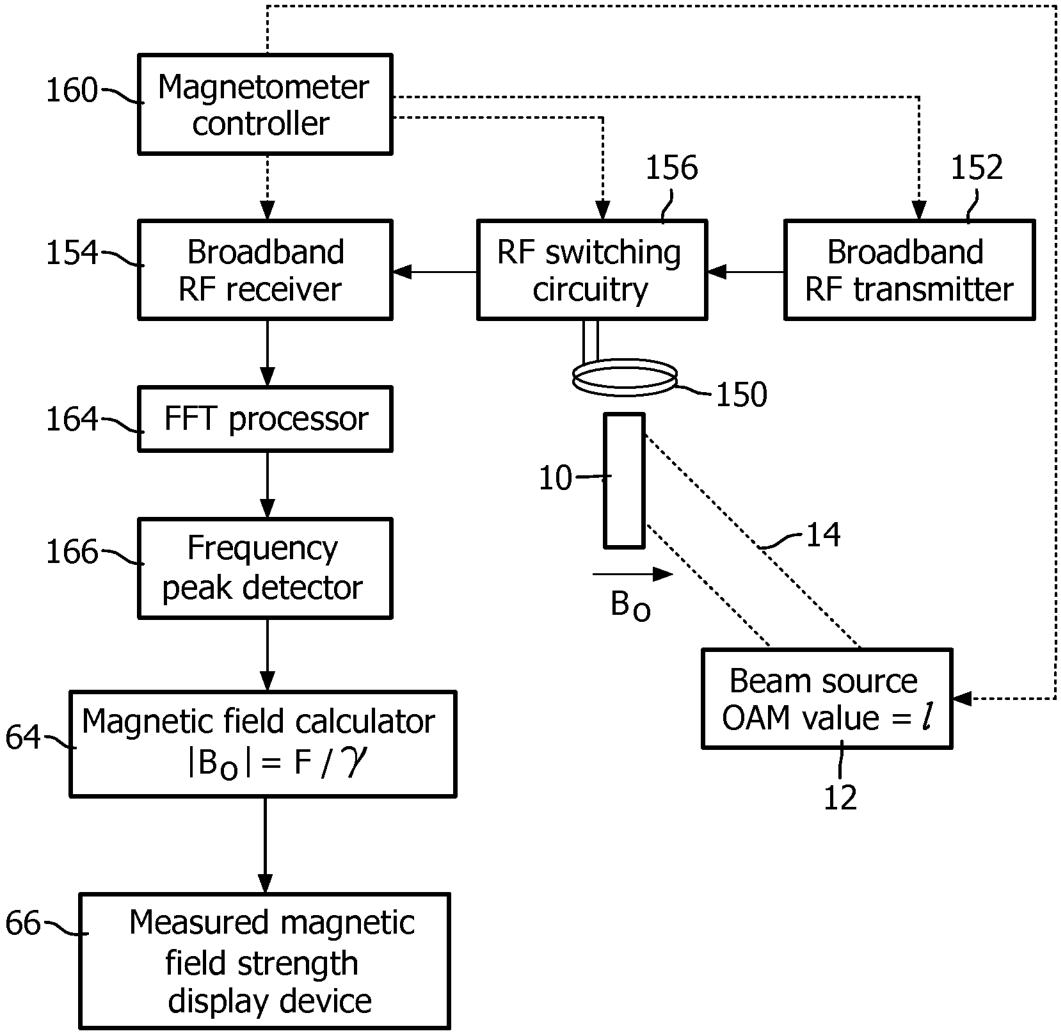
160
Magnetometer controller
154
Broadband RF receiver
156
RF switching circuitry
152
Broadband RF transmitter
150
164
FFT processor
10
14
166
Frequency peak detector
B0
Beam source OAM value = l
12
64
Magnetic field calculator |B0| = F / γ
66
Measured magnetic field strength display device

FIG. 4

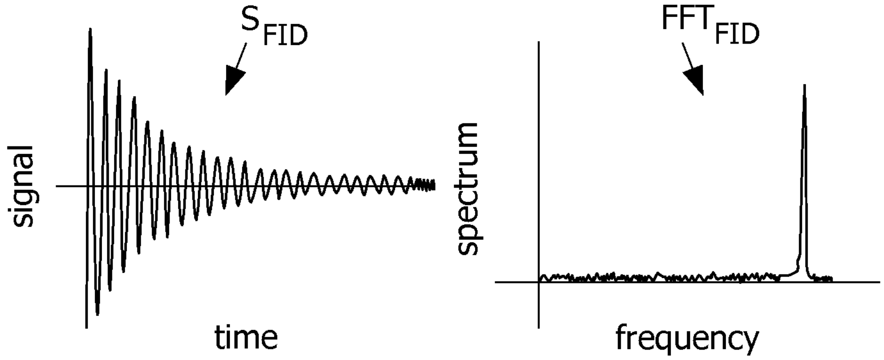

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/051144

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01R33/24
ADD.

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)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHOU ZHIJIAN ET AL: "Research on Magneto-dependent Sensor Applied to Optical Pumped Magnetometer", MEASURING TECHNOLOGY AND MECHATRONICS AUTOMATION (ICMTMA), 2010 INTERNATIONAL CONFERENCE ON, IEEE, PISCATAWAY, NJ, USA, 13 March 2010 (2010-03-13), pages 109-111, XP031672902, ISBN: 978-1-4244-5001-5 the whole document ----- -/--	1,12

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

☒ 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 filing 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 filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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 in the art.
"&" document member of the same patent family

Date of the actual completion of the international search 15 June 2011	Date of mailing of the international search report 27/06/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Raguin, Guy

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2011/051144

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BEVILACQUA G ET AL: "All-optical magnetometry for NMR detection in a micro-Tesla field and unshielded environment", JOURNAL OF MAGNETIC RESONANCE, ACADEMIC PRESS, ORLANDO, FL, US, vol. 201, no. 2, 1 December 2009 (2009-12-01), pages 222-229, XP026789707, ISSN: 1090-7807, DOI: DOI:10.1016/J.JMR.2009.09.013 [retrieved on 2009-09-22] the whole document -----	1,12
X	GROEGER S ET AL: "An improved laser pumped cesium magnetometer using hyperfine repumping", QUANTUM ELECTRONICS CONFERENCE, 2005. EQEC '05. EUROPEAN MUNICH, GERMANY 12-17 JUNE 2005, PISCATAWAY, NJ, USA,IEEE, 12 June 2005 (2005-06-12), pages 199-199, XP010873036, DOI: DOI:10.1109/EQEC.2005.1567366 ISBN: 978-0-7803-8973-1 the whole document -----	1,12
X	KERNEVEZ N ET AL: "Description of a high sensitivity CW scalar DNP-NMR magnetometer", IEEE TRANSACTIONS ON MAGNETICS, IEEE SERVICE CENTER, NEW YORK, NY, US, vol. 27, no. 6, 1 November 1991 (1991-11-01), pages 5402-5404, XP007918738, ISSN: 0018-9464, DOI: DOI:10.1109/20.278852X [retrieved on 2002-08-06] the whole document -----	1,12
T	WO 2009/090610 A1 (KONINKL PHILIPS ELECTRONICS NV [NL]; ALBU LUCIAN REMUS [US]; ELGORT DA) 23 July 2009 (2009-07-23) the whole document -----	
T	WO 2009/090609 A1 (KONINKL PHILIPS ELECTRONICS NV [NL]; ALBU LUCIAN REMUS [US]; MUKHERJEE) 23 July 2009 (2009-07-23) the whole document -----	
T	WO 2009/081360 A1 (KONINKL PHILIPS ELECTRONICS NV [NL]; ELGORT DANIEL R [US]; ALBU LUCIAN) 2 July 2009 (2009-07-02) the whole document -----	
	-/--	

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BOTTURA L ET AL: "Field Measurements", CAS - CERN ACCELERATOR SCHOOL ON SUPERCONDUCTIVITY AND CRYOGENICS FOR ACCELERATORS AND DETECTORS,, 8 May 2002 (2002-05-08), pages 1-34, XP007918723, cited in the application the whole document -----	1,12
A	SANTAMOTO: "Photon orbital angular momentum: problems and perspectives", FORTSCHR. PHYS., vol. 52, no. 11-12, 2004, pages 1141-53, XP007918722, cited in the application the whole document -----	1,12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2011/051144

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 2-11, 13-20(completely); 1, 12(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 2-11, 13-20(completely); 1, 12(partially)

1. The non-compliance with the substantive provisions of Art. 5 and 6 PCT (see below and section "Re Item VIII" of the WO-ISA) is to such an extent that a complete and meaningful search of claims 1-20 could not be carried out (Art. 17(2) PCT). 2. Lack of clarity (Art. 6 PCT): 2.1. The passage of claim 1, "an optical source configured to hyperpolarize the selected nuclear species of the sample by illuminating the sample with optical radiation having orbital angular momentum", appears to define nothing more than a mere result to be achieved (PCT/GL/ISPE 5.35) and therefore claim 1 appears to lack an essential feature required (Rule 6.3(a) PCT and PCT/GL/ISPE 5.33) in order to achieve the desired technical effect of "hyperpolariz[ing] the selected nuclear species of the sample". 2. Lack of sufficient disclosure (Art. 5 PCT): 2.1. It is noted that cited documents WO2009/081360, WO2009/090609 and WO2009/090610 were deemed to lack sufficient disclosure by the Search Authority and thus does not constitute a bona fide disclosure for a means to hyperpolarize selected nuclear species of atoms within any type of sample by illuminating the sample with optical radiation having orbital angular momentum (OAM). 2.2. More specifically, the application as a whole is silent with regards to e.g. which nuclei can be hyperpolarized by optical radiation having OAM, how to select the nuclei to be hyperpolarized, what is the relation between the local magnetic field to be measured and the experimental parameters (light spectrum, value of the OAM, duration of irradiation, ...), and how long the nuclear spins stay polarized. Therefore, the application as a whole lacks sufficient disclosure with respect to achieving the desired technical effects and the advantages listed on page 3, lines 15-18 of the description. 3. Given the above objections, a complete and meaningful search of claims 1-20 could not be carried out (Art. 17(2) PCT). Instead, the search ignored the features that have been insufficiently disclosed and/or are completely unclear. 3.1. More specifically, claim 1 was limited to the following: "An apparatus comprising: a magnetometer including: a sample comprising a selected nuclear species, an optical source configured to hyperpolarize the selected nuclear species of the sample by illuminating the sample with optical radiation, a radio frequency generator configured to input radio frequency energy to the hyperpolarized selected nuclear species of the sample over a probed range of radio frequencies, a detector configured to detect a frequency of nuclear magnetic resonance excited in the hyperpolarized selected nuclear species of the sample by the input radio frequency energy, and a signal output generator configured to output a signal indicative of magnetic field strength based on the detected frequency of nuclear magnetic resonance." Claim 12 was similarly limited. 2.2. Claims 2-11 and 13-20 were not searched at all.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2011/051144

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009090610 A1	23-07-2009	CN 101939638 A	05-01-2011
		EP 2235510 A1	06-10-2010
		JP 2011510288 T	31-03-2011
WO 2009090609 A1	23-07-2009	NONE	
WO 2009081360 A1	02-07-2009	CN 101971011 A	09-02-2011
		EP 2225551 A1	08-09-2010