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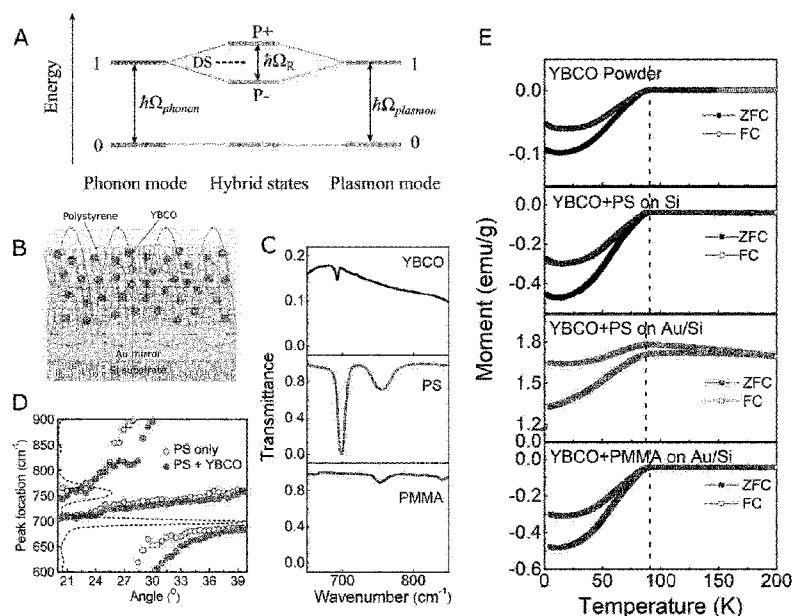


FIG. 1

(57) **Abstract:** The present invention concerns a method to modify the magnetic properties of a material comprising the steps of providing a reflective or photonic structure and of placing said material in or on said structure, said method being characterized in that it consists further in providing a structure which has an electromagnetic mode which is by design, or can be made by way of adjustment or tuning, resonant with a transition in said material and in controlling, in particular enhancing, the magnetism of said material, by means of strongly coupling said material to the local electromagnetic vacuum field and exploiting the formation of states of spatial extension exceeding the size of the grains of the material.



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Method to modify the magnetic properties of a material and device making
use of said method

The present invention is related to the field of the so called “strong coupling” and its possible practical uses and implementations.

More precisely, the invention concerns a method to modify the magnetic properties of a material, and also devices and machines using said
5 method.

Over the past decade, strong coupling has proven to be a promising way to modify and control properties of materials such as charge and energy transport (see references 1 to 13 quoted hereinafter), superconductivity (see references 14 to 16 quoted hereinafter), work
10 function(see reference 17 quoted hereinafter), non-linear optics (see references 18 to 21 quoted hereinafter) and chemical reactivity(see reference 22 quoted hereinafter). In strong coupling, the material is typically placed in the confined electromagnetic field of a cavity or a surface plasmon tuned to be in resonance with a material transition. Under the right conditions, new
15 hybrid light-matter states appear, called polaritonic states such as P^+ and P^- shown in Figure 1, modifying the ladder of energy levels of the material. Furthermore, this occurs even in the dark due to the interaction between the zero-point energy fluctuations of both the optical mode and the material.

Strong coupling is facilitated by collective coupling whereby a
20 large number N of oscillators such as molecules couple to a single optical mode. This enhances the Rabi splitting $\hbar\Omega_R$, the energy that separates the polaritonic states P^+ and P^- , as $\sqrt{N}$. In addition, $N-1$ so-called dark states (DS) are formed. P^+ , P^- and DS are all collective states, delocalized over the optical mode volume (Figure 1A).

25 In the course of studying the effects of strong coupling of phonons on superconducting microcrystalline powders, the inventors found that in parallel to the superconductivity another property was being surprisingly modified by strong coupling, namely the magnetic response.

Thus, in a first and main aspect, the present invention concerns
30 a method to modify the magnetic properties of a material comprising the steps of providing a reflective or photonic structure and of placing said material in or on said structure,

said method being characterized in that it consists further in providing a structure which has an electromagnetic mode which is by design, or can be made by way of adjustment or tuning, resonant with a transition in said material and in controlling, in particular enhancing, the magnetism of said material, by means of strongly coupling said material to the local electromagnetic vacuum field and exploiting the formation of states of spatial extension exceeding the size of the grains of the material.

Materials to be considered in relation to the invention are inorganic materials, especially in the form of nanoparticles exhibiting ferromagnetism. They comprise in particular inorganic oxides. Typical examples of such nanomaterials are the following oxides: CeO₂, TiO₂, Al₂O₃, and MgO.

Nanoparticles of nitrides such as GaN and chalcogenides such as CdS and CdSe also exhibit ferromagnetism and may thus also be considered as candidate materials for the invention.

Furthermore, it can also be envisaged to modify/enhance the ferromagnetism of magnetic semiconductor materials by means of the invention.

The present invention may also show one or several of the following possible additional features, or exploit one or several of the following embodiments:

- the Q-factor, defined as the ratio of the wavelength of the resonance divided by the half-width of the resonance, of the resonant electromagnetic mode is comprised between 10 and 1 000, preferably between 10 and 100;

- the electromagnetic mode is a surface plasmon mode;

- the electromagnetic mode is a cavity mode;

- the cavity mode is defined by two opposed mirror structures, preferably two parallel planar mirrors;

- the reflective structure comprises at least one metallic surface, for example made of a metal film or of two opposed metal films;

- the concerned transition of the material is an electronic transition;

- the concerned transition of the material is a vibrational or phonon transition;

- the material is strong coupled by a cooperative coupling process involving another material.

In the context of a first implementation, the method may consist, by means of coupling to local electromagnetic vacuum field and exploiting the resulting rearrangement of the energy levels of the material, in inducing the formation of collective hybrid light-matter states in the material in order to increase the magnetism extending over a large number of grains of the material, preferably over an area extending at least 100 nm in all directions.

In the context of an other implementation, the method may consist, by means of coupling to local electromagnetic vacuum field and exploiting the resulting rearrangement of the energy levels of nanoparticles, in inducing the formation of collective hybrid light-matter states in nanoparticles in order to increase the temperature at which the magnetism persists, preferably above room temperature.

In relation to possible practical constructive embodiments making use of the inventive method, said latter may be applied in a functional device comprising said reflective or photonic structure, said device being preferably one of a spintronic device, a magnetic device or a magneto-sensing device.

According to a second aspect, the invention also encompasses a spintronic, a magnetic or magneto-sensing device comprising a material located in or on a reflective or photonic structure,

said device being characterized in that said structure has an electromagnetic mode which is by design or can be made by way of adjustment or tuning, resonant with a transition in said material and in controlling, in particular enhancing, the magnetism in said material, by means of strongly coupling said material to the local electromagnetic vacuum field and exploiting the formation of extended macroscopic states in said material, namely states of spatial extension exceeding the size of the grains of said material.

The device according to the present invention may also show one or several of the following possible additional features, or correspond to one or several of the following embodiments:

- the concerned transition in the given material is one of an electronic, a vibrational or a phonon transition;

- the reflective or photonic structure comprises plasmonic structures, the electromagnetic mode being a surface plasmon mode;

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- the reflective or photonic structure consists of an optical microcavity, preferably a Fabry-Perot cavity, the electromagnetic mode being a cavity mode;

5 - the reflective structure comprises two metallic or dielectric mirrors forming with the material a sandwich structure, the distance between said mirrors being adjusted to resonate with a transition in said material.

According to a third aspect, the invention also concerns a machine or apparatus able and intended to perform at least one magnetic function, wherein said machine or apparatus comprises at least one device as
10 mentioned before, said device being designed to perform the method to modify the magnetic properties of a material as described.

The invention will be better understood in relation to the description below, which relates to a possible embodiment, given by way of a non-limiting example showing the effects of the principle underlying the
15 invention.

More precisely, the invention will be explained by way of experimental results in relation to YBCO, with reference to the accompanying drawings, comprising figures 1 to 6 in which respectively:

Figure 1 (A) is a schematic illustration of the strong coupling
20 (cooperative) between the phonon mode of the YBCO and the surface plasmon mode of Au film. The hybrid states P^+ and P^- are separated by the Rabi splitting energy, and the dark states (DS) are represented by the black dashed lines.

Figure 1 (B) is a cartoonic/schematic illustration of the
25 cooperatively strongly coupled YBCO nanoparticles embedded in the polymer matrix. The YBCO containing polystyrene is spin coated on to the Au (10 nm) film sputtered on the Si window. The polystyrene (PS) matrix is shown in green and the embedded YBCO nanoparticles are shown as black circles.

30 Figure 1 (C) is a FT-IR transmission spectra of the YBCO particles (black curve-top curve), PS (red curve-middle curve) and PMMA (blue curve-bottom curve).

Figure 1 (D) shows dispersion curves showing the cooperative
35 strong coupling of the surface plasmon mode with the PS vibration at 697 cm^{-1} which overlaps with the YBCO phonon mode. The empty red circles represent the strong coupling for PS alone, and the solid (filled) circles shows

the PS+YBCO mixture. The PS transmission spectrum is shown by the black dashed curve.

Figure 1 (E) illustrates the temperature-dependent magnetization of the YBCO powder (black circles-top curves), film of YBCO+PS on Si (black squares-curves second from top), strongly coupled YBCO+PS on Au/Si (red squares-curves third from top) and cooperatively off-resonant YBCO+PMMA on Au/Si (blue squares-bottom curves) in the zero-field-cooled (ZFC; filled squares and circles) and 100 Oe field-cooled (FC; empty squares and circles) modes in the temperature range of 4K to 200K. The onset of superconducting transition (T_c) was determined from the intersection point of the polynomial fits on the ZFC and FC curves. The bare film features a T_c of 92 K, while it is shifted to 87 K for the strongly coupled YBCO as shown by the dashed lines in the respective panels.

Figure 2 illustrates by means of four pairs of comparative curves the magnetic response of the YBCO at 10K and 300K for various conditions: (A) the original powder, (B) the YBCO dispersed in PS on Si substrate, (C) on Au coated Si substrate, and (D) the same as the latter for YBCO dispersed in PMMA.

Figure 3 illustrates by way of three graphical charts (A-C) the comparison of the $M(H)$ curves of the strongly coupled YBCO (YBCO+PS on Au/Si; red filled circles) and YBCO powder (black empty circles) at temperatures near the superconducting transition of YBCO; (A) 50K, (B) 80K and (C) 100K.

Figure 4 (A) shows the $M(H)$ curves of YBCO at 300K for varying Au thickness: 20 nm (red squares), 60 nm (green circles) and 100 nm (blue diamonds).

Figure 4 (B) is a cartoon/schematic representation of the domain structure of the polymer matrix containing YBCO on Si with the magnetic spins in each domain oriented in differently and the possible alignment of the magnetic spins under strong coupling resulting in the enhanced ferromagnetism.

Figure 5 illustrates the $M(H)$ curves of Rb_3C_{60} at 10K, 35K and 300K: (A), (B) and (C) in powder form without coupling, and (D), (E) and (F) under strong coupling where Rb_3C_{60} is dispersed in polystyrene (PS) on Au/Si substrate. All the latter curves have been corrected for the diamagnetic signal of the Si substrate.

Figure 6 is a mixed schematical and graphical representation showing the enhancement of ferro-magnetism of strongly coupled YBCO nanoparticles with comparison to non coupled identical apticles (NB: the scale -red- on the left side of the graphical chart applies to the strongly coupled YBCO nanoparticles- pronounced S curve- whereas the scale -black- on the right side of the graphical chart applies to non coupled YBCO nanoparticles-flat S curve).

As indicated before, a non limitative example showing the effects of the principle underlying the invention by way of experiments, is described and illustrated hereinafter, in relation to YBCO and with respect to figures 1 to 5.

YBCO bulk material is a well-known spin singlet superconductor which exhibits in the normal state antiferromagnetic short-range correlations. However, for nanoparticle (NP) samples, unexpected room temperature ferromagnetism, with a well-defined hysteresis cycle, has been reported which is believed to be related to the presence of oxygen vacancies created at the surface of NPs (see references 26 to 32 quoted hereinafter). Such a behavior has given rise to a huge number of studies of oxides, nitrides or sulfides, expected to be non-magnetic but which exhibit room temperature ferromagnetism when they are dispersed at the nanoscale.

The net moment is usually very low, and accordingly can be attributed to magnetic impurities, but several reliable experimental and DFT-based theoretical studies conclude that it is likely intrinsic and due to oxygen vacancies (see references 27 and 33 quoted hereinafter). For instance, a direct magnetic imaging of the non-magnetic SrTiO_3 fully supports this assumption (see reference 30 quoted hereinafter). By using ultrahigh resolution photoemission electron microscopy (PEEM), it was shown that ferromagnetic nanodomains develop at the oxygen-deficient surface of the sample, even for temperatures well above 300K, confirming the existence of intrinsic ferromagnetism.

Now, the inventors have noticed that under collective strong coupling this ferromagnetism is enhanced by over two orders of magnitude to the point that it even can perturb the superconductivity and lower the T_c of YBCO. There are several parameters that are critical to observe such an enhancement in the ferromagnetism. They can be rationalized by the collective states that favor spin alignment and increase the magnetic domain size.

Since YBCO has phonons modes that are weakly absorbing, the best way to strongly couple this material to the surface plasmon mode of Au films is to use the cooperative coupling technique illustrated in Figure 1B. In this approach, the material to be coupled is placed in a polymer matrix which
5 has a strong vibrational band that overlaps one of the YBCO phonon bands. The polymer vibrational band is strongly coupled and transfers the coupling property to the material thru a cooperative process described in detail elsewhere (see references 34 and 35 quoted hereinafter). This technique works well for molecular solutions and fine powders as in the present study
10 where the average particle size is around 200 nm. This cooperative regime generates extended states that favors long-distance interaction between particles.

The samples were prepared using commercial YBCO powder purchased from Can Superconductors. X-ray diffraction pattern shows that
15 the YBCO has, as expected, the orthorhombic structure (i.e. the 123 phase) and that there is a very small amount of the green phase Y_2BaCuO_5 . Note that this extra phase does not affect the magnetic properties nor the superconducting transition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ at 92 K. The YBCO was further ground in a mortar before mixing it with a polymer solution (either
20 polystyrene, PS, or polymethylmethacrylate, PMMA). The mixed solution was then spin coated on sputtered Au film deposited on a high purity Si substrate. The Au film supports the surface plasmons that couple to the material vibrational band (Figure 1B). The FTIR data for the powder used in this study is shown in Figure 1C together with those of the PS and PMMA.
25 The 697 cm^{-1} phonon band of YBCO is cooperatively coupled, using the overlap with the vibrational mode of PS (Figure 1C). The corresponding dispersion curve of the strongly coupled sample with surface plasmon is shown in Figure 1D. PMMA which has no bands that overlap with YBCO phonon mode was used as a reference.

As also shown in figures 1, the T_c of YBCO only shifts to lower
30 temperatures when the sample is cooperatively coupled using PS, as shown in Figure 1E. In addition to the T_c shift, notice the positive magnetic moment in this condition and the difference between the FC and ZFC curves above T_c , due to the appearance of the enhanced ferromagnetism under cooperative
35 strong coupling.

It should be noted that the IR spectrum of YBCO is dependent on the origin of the sample and how it was prepared. For instance, the YBCO

peak at 697 cm^{-1} which is coupled in these experiments has been attributed to an apical oxygen stretching mode of the crystal structure (see references 36 and 37 quoted hereinafter), but it could also arise from the small amount carbon retention during the fabrication of YBCO, which generates a barium carbonate (BaCO_3) type environment. The latter results from the incorporation of C in the YBCO structure and is mainly associated with the surface as shown in several studies (see references 38 and 39 quoted hereinafter), and disappears upon high temperature annealing in an inert atmosphere. X-ray Photoelectron Spectroscopy (XPS) confirms that the YBCO in this study contains a small amount of BaCO_3 . Since the T_c of the used bare powder is 92 K, it indicates that nevertheless the carbon content is less than 0.04%, according to the literature (see reference 40 quoted hereinafter),

In relation to Figure 2, $M(H)$ curves of YBCO are illustrated both at 10 K and 300K: (A) YBCO powder; inset in the bottom panel gives the zoom of the $M(H)$ at 300K showing the weakly ferromagnetic character of the powder (B) thin film of YBCO+PS on Si (C) strongly coupled thin film of YBCO+PS on Au/Si and (D) cooperatively off-resonant thin film of YBCO+PMMA on Au/Si. All the curve, except the powder (A), have been corrected for the diamagnetic signal of the Si substrate.

The $M(H)$ curves at 10K, for samples A, B and D, exhibit the typical butterfly-like behavior of the superconducting YBCO phase. The minimum of magnetization, at 0.1 T, is the critical field beyond which the field penetrates the sample. It agrees well with previous findings which range between 100 and 200mT depending on the material (see references 41 and 42 quoted hereinafter). In turn, when using PS as polymer matrix (Figure 2C), a striking change of $M(H)$ occurs, since a ferromagnetic behavior takes place with a saturation value of about $0.90\text{ }\mu\text{B/mol}$, and a coercive field of 40mT at 10K. At 300K, the pure YBCO powder (sample A) exhibits a paramagnetic behavior with a weak ferromagnetic component detected at low field, but which is much weaker than for the strongly coupled sample (YBCO in PS matrix on Au/Si). Note that the uncoupled samples B and D show at 300K very similar $M(H)$ variations to that of powder sample A.

What is most striking and unexpectedly achieved in these experiments is that the magnetic moment is enhanced by a factor 300 times under collective strong coupling at room temperature. The observed magnetic moment of $0.90\text{ }\mu\text{B/mol}$ is very large and cannot be explained by

assuming that it originates only from anion vacancies at the surface of YBCO NPs since less than 1% of the YBCO unit cells are at the surface. As a result, the contribution of inner NPs oxygen vacancies must be considered. Furthermore, it is not realistic to explain the ferromagnetic contribution at room temperature by the presence of NPs metallic impurities since then their size would have to be several tens of nanometers to remain magnetic at such temperatures. Accordingly, they would be detected by EDAX, XRD and XPS, contrary to the findings of the inventors.

When the same YBCO is dispersed in PMMA on the Au surface, no enhancement of the magnetism is detectable, as expected, since the cooperative coupling is not possible for this polymer confirming the key role of strong coupling in generating the ferromagnetic enhancement.

When considering figure 3, the plots shown illustrate the striking and unexpected change of magnetic behavior between uncoupled (powder) and strongly coupled YBCO samples for 3 different temperatures. While the powder sample shows a significant change of $M(H)$ above T_c , the strongly coupled one is dominated by a ferromagnetic-like behavior whatever temperature. At 80K, namely just below T_c , it can be observed that a small ferromagnetic component already exists in the powder sample, which competes with superconducting state, and that this component is multiplied by at least two orders of magnitude in the strongly coupled system.

Since the strong coupling involves the surface plasmons of the Au film, the inventors also studied the effect of the Au film thickness as shown in Figure 4. The hysteretic behavior and, in particular, the net moment of the magnetization increase with the Au thickness and saturates above 100 nm. This is related to the quality of the optical response of the Au film which is known to improve in this thickness range (see reference 43 quoted hereinafter). It confirms the role of the strong coupling induced hybridization between the phonons and the surface plasmons in enhancing the magnetic response.

Similarly to dilute ferromagnetic oxides (see references 27, 44 and 45 quoted hereinafter), shallow donor electrons, related to oxygen vacancies, form magnetic polarons that mediate magnetic ordering. However, both the very high ordering temperature, above 300K, and the significant magnetic moment ($0.90 \mu_B/\text{mol}$) make such a model unrealistic to explain the experimental results. Note that this also rules out the effect of impurities made of transition metal oxide or pure metal nanoparticles. As a

result, surface states alone can no longer be involved to explain the magnetic behavior and a model based on the effect of a strong coupling between plasmons, generated in the bulk YBCO compound, and spin carriers must be considered.

5 Ferromagnetic domains already exist in pure nanosized YBCO powder, due to oxygen vacancies, and it has been well-established that they can coexist with superconductivity when the magnetic field is less than a threshold value H^* beyond which Cooper pairs are destroyed (see references 28 and 29 quoted hereinafter). These magnetic domains would be related to
10 a hopping mechanism of the unpaired electrons like that reported for dilute magnetic semiconductors. Such a mechanism is well known in mixed valence systems where the transfer of an excess electron between neighboring sites is allowed only for parallel spin configurations of the valence electrons (see references 46 to 48 quoted hereinafter). Then, ferromagnetism is promoted.
15 The magnitude of the coupling being given by the transfer integral (of the order of 103K), very high ordering temperatures are expected, as observed for YBCO NP powders ($T_{\text{Curie}} > 300\text{K}$).

Under strong coupling, the behavior of YBCO NPs exhibits striking and unexpected variation as evidenced by the magnetic moment that
20 is boosted by orders of magnitude and remains so even at room temperature. Then, the competition with the superconducting states below T_c appears crucial because of the antagonism between both properties. A description of the behavior necessitates introducing the coupling between electronic states and phonon modes of the network. At very low temperature, the growth of
25 magnetic domains is most likely collective and related to the breaking of Cooper pairs for an increasing external field. The delocalization of the unpaired electrons then promotes nanodomains to line up in the field direction which in turn reinforces existing ferromagnetic domains. In this process, coherent phonon modes induced by the strong coupling play a major
30 role. In turn, when decreasing field below H^* , the spins condense into Cooper pairs progressively so as to form the superconducting nanodomains but this recombination is limited by the internal field of the ferromagnetic domains.

At high temperatures, only ferromagnetic domains remain. The variation of the net moment at 300K, from 0.037 to 0.22 $\mu\text{B/mol}$ for Au
35 thickness ranging from 20 to 100 nm, confirms the key role of plasmon resonance in the growth of magnetic domains. Furthermore, the value of the

magnetic moment points out that the inner spins participate in the magnetic ordering and is not limited to the NPs surface.

Finally, the existence of ferromagnetism at room temperature makes such systems suitable for the practical development of next generations of spintronic nanodevices. Usually, the limitation in NPs magnetic materials stems from the fact that they are characterized by low temperature blocking temperature. Strong coupling of NPs materials such as YBCO may be promising solution to get around this limitation. The experimental results obtained by the inventors, together with the recent theoretical prediction of enhanced ferro-electric phase transition (see references 49 quoted hereinafter), further broadens the appeal of strong coupling with the vacuum field to engineer material properties.

Additional information concerning the invention is disclosed in: “Large enhancement of ferro-Magnetism under Collective Strong Coupling of YBCO Nanoparticles”, Anoop Thomas et al., Nanoletters, 2021, the content of which is incorporated herein by reference.

List of bibliographic references quoted previously:

- (1) Orgiu, E.; George, J.; Hutchison, J. A.; Devaux, E.; Dayen, J. F.; Doudin, B.; Stellacci, F.; Genet, C.; Schachenmayer, J.; Genes, C.; Pupillo, G.; Samori, P.; Ebbesen, T. W. Conductivity in Organic Semiconductors Hybridized with the Vacuum Field. *Nat. Mater.* **2015**, *14*, 1123–1129.
- (2) Hagenmüller, D.; Schachenmayer, J.; Schütz, S.; Genes, C.; Pupillo, G. Cavity-Enhanced Transport of Charge. *Phys. Rev. Lett.* **2017**, *119*, 223601.
- (3) Bartolo, N.; Ciuti, C. Vacuum-Dressed Cavity Magneto-Transport of a Two-Dimensional Electron Gas. *Phys. Rev. B* **2018**, *98*, 205301.
- (4) Paravicini-Bagliani, G. L.; Appugliese, F.; Richter, E.; Valmorra, F.; Keller, J.; Beck, M.; Bartolo, N.; Rössler, C.; Ihn, T.; Ensslin, K.; Ciuti, C.; Scalari, G.; Faist, J. Magneto-Transport Controlled by Landau Polariton States. *Nat. Phys.* **2019**, *15*, 186–190.
- (5) Krainova, N.; Grede, A. J.; Tsokkou, D.; Banerji, N.; Giebink, N. C. Polaron Photoconductivity in the Weak and Strong Light-Matter Coupling Regime. *Phys. Rev. Lett.* **2020**, *124*, 177401.

- (6) Nagarajan, K.; George, J.; Thomas, A.; Devaux, E.; Chervy, T.; Azzini, S.; Joseph, K.; Jouaiti, A.; Hosseini, M.W.; Kumar, A.; Genet, C.; Bartolo, N.; Ciuti, C.; Ebbesen, T.W. Conductivity and Photoconductivity of a p-Type organic Semiconductor under Ultra-Strong Coupling. *ACS Nano* **2020**, *14*, 10219-10225.
- (7) Gonzalez-Ballester, C.; Feist, J.; Moreno, E.; Garcia-Vidal, F. J. Harvesting Excitons through Plasmonic Strong Coupling. *Phys. Rev. B* **2015**, *92*, 121402.
- (8) Coles, D. M.; Somaschi, N.; Michetti, P.; Clark, C.; Lagoudakis, P. G.; Savvidis, P. G.; Lidzey, D. G. Polariton-Mediated Energy Transfer between Organic Dyes in a Strongly Coupled Optical Microcavity. *Nat. Mater.* **2014**, *13*, 712–719.
- (9) Zhong, X.; Chervy, T.; Zhang, L.; Thomas, A.; George, J.; Genet, C.; Hutchison, J. A.; Ebbesen, T. W. Energy Transfer between Spatially Separated Entangled Molecules. *Angew. Chem. Int. Ed.* **2017**, *56*, 9034–9038.
- (10) Akulov, K.; Bochman, D.; Golombek, A.; Schwartz, T. Long-Distance Resonant Energy Transfer Mediated by Hybrid Plasmonic–Photonic Modes. *J. Phys. Chem. C* **2018**, *122*, 15853–15860.
- (11) Feist, J.; Garcia-Vidal, F. J. Extraordinary Exciton Conductance Induced by Strong Coupling. *Phys. Rev. Lett.* **2015**, *114*, 196402.
- (12) Schachenmayer, J.; Genes, C.; Tignone, E.; Pupillo, G. Cavity-Enhanced Transport of Excitons. *Phys. Rev. Lett.* **2015**, *114*, 196403.
- (13) Rozenman, G. G.; Akulov, K.; Golombek, A.; Schwartz, T. Long-Range Transport of Organic Exciton-Polaritons Revealed by Ultrafast Microscopy. *ACS Photonics* **2018**, *5*, 105–110.
- (14) Thomas, A.; Devaux, E.; Nagarajan, K.; Chervy, T. ; Seidel, M. ; Hagenmüller, D. ; Schütz, S. ; Schachenmayer, J. ; Genet, C., Pupillo, G.; Ebbesen, T.W. Exploring Superconductivity under Strong coupling with the Vacuum Electromagnetic Field. *ArXiv191101459 Cond-Mat Physicsquant-Ph* **2019**
- (15) Sentef, M. A.; Ruggenthaler, M.; Rubio, A. Cavity Quantum-Electrodynamical Polaritonically Enhanced Electron-Phonon Coupling and Its Influence on Superconductivity. *Sci. Adv.* **2018**, *4*, eaau6969.
- (16) Schlawin, F.; Cavalleri, A.; Jaksch, D. Cavity-Mediated Electron-Photon Superconductivity. *Phys. Rev. Lett.* **2019**, *122*, 133602.

- (17) Hutchison, J. A.; Liscio, A.; Schwartz, T.; Canaguier-Durand, A.; Genet, C.; Palermo, V.; Samori, P.; Ebbesen, T.W. Tuning the Work-Function via Strong Coupling. *Adv. Mater.* **2013**, *25*, 2481-2485.
- 5 (18) Chervy, T.; Xu, J.; Duan, Y.; Wang, C.; Mager, L.; Frerejean, M.; Münnhoff, J. A. W.; Tinnemans, P.; Hutchison, J. A.; Genet, C.; Rowan, A. E.; Rasing, T.; Ebbesen, T. W. High-Efficiency Second-Harmonic Generation from Hybrid Light-Matter States. *Nano Lett.* **2016**, *16*, 7352–7356.
- 10 (19) Barachati, F.; Simon, J.; Getmanenko, Y. A.; Barlow, S.; Marder, S. R.; Kéna-Cohen, S. Tunable Third-Harmonic Generation from Polaritons in the Ultrastrong Coupling Regime. *ACS Photonics* **2018**, *5*, 119–125.
- (20) Liu, B.; Crescimanno, M.; Twieg, R. J.; Singer, K. D. Dispersion of Third-Harmonic Generation in Organic Cavity Polaritons. *Adv. Opt. Mater.* **2019**, *7*, 1801682.
- 15 (21) Wang, K.; Seidel, M.; Nagarajan, K.; Chervy, T.; Genet, C.; Ebbesen, T.W. Large Optical Nonlinearity Enhancement under Electronic Strong Coupling. *Nat. Commun.* **2021**, In press
- (22) Ebbesen, T. W. Hybrid Light–Matter States in a Molecular and Material Science Perspective. *Acc. Chem. Res.* **2016**, *49*, 2403–2412.
- 20 (23) Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. Theory of Superconductivity. *Phys. Rev.* **1957**, *108*, 1175–1204.
- (24) Zhao, G.; Hunt, M. B.; Keller, H.; Müller, K. A. Evidence for Polaronic Supercarriers in the Copper Oxide Superconductors $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. *Nature* **1997**, *385*, 236–239.
- 25 (25) Schneider, T.; Keller, H. Universal Trends in Extreme Type-II Superconductors. *Phys. Rev. Lett.* **1992**, *69*, 3374–3377.
- (26) Shipra; Gomathi, A.; Sundaresan, A.; Rao, C. N. R. Room-Temperature Ferromagnetism in Nanoparticles of Superconducting Materials. *Solid State Commun.* **2007**, *142*, 685–688.
- 30 (27) Sundaresan, A.; Rao, C. N. R. Ferromagnetism as a Universal Feature of Inorganic Nanoparticles. *Nano Today* **2009**, *4*, 96–106.
- (28) Hasanain, S. K.; Akhtar, N.; Mumtaz, A. Particle Size Dependence of the Superconductivity and Ferromagnetism in YBCO Nanoparticles. *J. Nanoparticle Res.* **2011**, *13*, 1953–1960.

- (29) Gasmi, M.; Khene, S.; Fillion, G. Coexistence of Superconductivity and Ferromagnetism in Nanosized YBCO Powders. *J. Phys. Chem. Solids* **2013**, *74*, 1414–1418.
- 5 (30) Taniuchi, T.; Motoyui, Y.; Morozumi, K.; Rödel, T. C.; Fortuna, F.; Santander-Syro, A. F.; Shin, S. Imaging of Room-Temperature Ferromagnetic Nano-Domains at the Surface of a Non-Magnetic Oxide. *Nat. Commun.* **2016**, *7*, 11781.
- 10 (31) Pemmaraju, C.D.; Sanvito, S. Ferromagnetism driven by intrinsic point defects in HfO₂. *Phys. Rev. Lett.* **2005**, *94*, 217205
- (32) Zhang, Z.H.; Wang, X.; Xu, J.B.; Muller, S.; Ronning, C.; Li, Q.; Evidence of intrinsic ferromagnetism in individual dilute magnetic semiconducting nanostructures. *Nature Mater.* **2009**, *4*, 523–527
- 15 (33) Sharma, P.; Gupta, A.; Rao, K.V.; Owens, F.J.; Sharma, R.; Ahuja, R.; Osorio Guillen, J.M.; Johansson, B.; Gehring, G.A. Ferromagnetism above room temperature in bulk and transparent thin films of Mn-doped ZnO. *Nature Mater.* **2003**, *2*, 673–677.
- 20 (34) Lather, J.; Bhatt, P.; Thomas, A.; Ebbesen, T. W.; George, J. Cavity Catalysis by Cooperative Vibrational Strong Coupling of Reactant and Solvent Molecules. *Angew. Chem. Int. Ed.* **2019**, *58*, 10635–10638.
- (35) Schütz, S.; Schachenmayer, J.; Hagenmüller, D.; Brennen, G. K.; Volz, T.; Sandoghdar, V.; Ebbesen, T. W.; Genes, C.; Pupillo, G. Ensemble-Induced Strong Light-Matter Coupling of a Single Quantum Emitter. *Phys. Rev. Lett.* **2020**, *124*, 113602.
- 25 (36) Arai, M.; Yamada, K.; Hidaka, Y.; Itoh, S.; Bowden, Z. A.; Taylor, A. D.; Endoh, Y. Anomaly of Phonon State of Superconducting YBa₂Cu₃O₇ Studied by Inelastic Neutron Scattering. *Phys. Rev. Lett.* **1992**, *69*, 359–362.
- 30 (37) Calvani, P.; Capizzi, M.; Lupi, S.; Balestrino, G. Infrared Active Vibrational Modes Strongly Coupled to Carriers in High-Tc Superconductors. *Europhys. Lett. EPL* **1995**, *31*, 473–478.
- (38) Shaw, T. M.; Dimos, D.; Batson, P. E.; Schrott, A. G.; Clarke, D. R.; Duncombe, P. R. Carbon Retention in YBa₂Cu₃O_{7-δ} and Its Effect on the Superconducting Transition. *J. Mater. Res.* **1990**, *5*, 1176–1184.
- 35 (39) Wang, J.; Monot, I.; Hervieu, M.; Provost, J.; Desgardin, G. Evidence of Carbon Retention in Ceramics and Its Effect on the Superconducting Properties. *Supercond. Sci. Technol.* **1996**, *9*, 69–75.

- (40) Masuda, Y.; Ogawa, R.; Kawate, Y.; Matsubara, K.; Tateishi, T.; Sakka, S. The Effect of Residual Carbon on the Superconducting Properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Powders. *J. Mater. Res.* **1993**, *8*, 693–698.
- 5 (41) D. -X. Chen, R.B. Goldfarb, R.W. Cross, A. Sanchez, Surface barrier and lower critical field in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ superconductors. *Phys. Rev. B*, **1993**, *48*, 6426-6430.
- (42) Buntar, V.; Riccò, M.; Cristofolini, L.; Weber, H. W.; Bolzoni, F. Critical Fields of the Superconducting Fullerene $\text{RbCs}_2\text{C}_{60}$. *Phys. Rev. B* **1995**, *52*, 4432–4437.
- 10 (43) Fontana, E. Thickness Optimization of Metal Films for the Development of Surface-Plasmon-Based Sensors for Nonabsorbing Media. *Appl. Opt.* **2006**, *45*, 7632–7642.
- (44) Venkatesan, M.; Fitzgerald, C. B.; Coey, J. M. D. Unexpected Magnetism in a Dielectric Oxide. *Nature* **2004**, *430*, 630–630.
- 15 (45) Hong, N. H.; Sakai, J.; Poirot, N.; Brizé, V. Room-Temperature Ferromagnetism Observed in Undoped Semiconducting and Insulating Oxide Thin Films. *Phys. Rev. B* **2006**, *73*, 132404.
- (46) Anderson, P. W.; Hasegawa, H. Considerations on Double Exchange. *Phys. Rev.* **1955**, *100*, 675–681.
- 20 (47) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. Electron Delocalization in Mixed-Valence Molybdenum Polyanions. *J. Am. Chem. Soc.* **1982**, *104*, 3194–3202.
- (48) Drillon, M.; Pourroy, G.; Darriet, J. Electronic and Vibronic Coupling in a Mixed-Valence Dimeric Unit d^1-d^2 , Magnetic Aspects. *Chem. Phys.* **1984**, *88*, 27–37.
- 25 (49) Ashida, Y.; İmamoğlu, A.; Faist, J.; Jaksch, D.; Cavalleri, A.; Demler, E. Quantum Electrodynamical Control of Matter: Cavity-Enhanced Ferroelectric Phase Transition. *Phys. Rev. X* **2020**, *10*, 041027.

Of course, the invention is not limited to the at least one
30 embodiment described and represented in the accompanying drawings. Modifications remain possible, particularly from the viewpoint of the composition of the various elements or by substitution of technical equivalents without thereby exceeding the field of protection of the invention.

CLAIMS

1. A method to modify the magnetic properties of a material comprising the steps of providing a reflective or photonic structure and of placing said material in or on said structure,

said method being characterized in that it consists further in
5 providing a structure which has an electromagnetic mode which is by design, or can be made by way of adjustment or tuning, resonant with a transition in said material and in controlling, in particular enhancing, the magnetism of said material, by means of strongly coupling said material to the local
10 electromagnetic vacuum field and exploiting the formation of states of spatial extension exceeding the size of the grains of the material.

2. A method according to claim 1, characterized in that the Q-factor, defined as the ratio of the wavelength of the resonance divided by the half-width of the resonance, of the resonant electromagnetic mode is comprised between 10 and 1 000, preferably between 10 and 100.

15 3. A method according to claim 1, characterized in that the electromagnetic mode is a surface plasmon mode.

4. A method according to claim 1, characterized in that the electromagnetic mode is a cavity mode.

20 5. A method according to claim 4, characterized in that the cavity mode is defined by two opposed mirror structures, preferably two parallel planar mirrors.

6. A method according to claim 1, characterized in that the reflective structure comprises at least one metallic surface, for example made of a metal film or of two opposed metal films.

25 7. A method according to claim 1, characterized in that the concerned transition of the material is an electronic transition.

8. A method according to claim 1, characterized in that the concerned transition of the material is a vibrational or phonon transition.

30 9. A method according to claim 1, characterized in that said material is strong coupled by a cooperative coupling process involving another material.

10. A method according to anyone of claims 1 to 9, characterized in that it consists, by means of coupling to local electromagnetic vacuum field and exploiting the resulting rearrangement of the energy levels of the

material, in inducing the formation of collective hybrid light-matter states in the material in order to increase the magnetism extending over a large number of grains of the material, preferably over an area extending at least 100 nm in all directions.

5 11. A method according to anyone of claims 1 to 9, characterized in that it consists, by means of coupling to local electromagnetic vacuum field and exploiting the resulting rearrangement of the energy levels of nanoparticles, in inducing the formation of collective hybrid light-matter states in nanoparticles in order to increase the temperature at which the magnetism persists, preferably above room temperature.

10 12. A method according to anyone of claims 1 to 11, characterized in that it is applied in a functional device comprising said reflective or photonic structure, said device being one of a spintronic device, a magnetic device or a magneto-sensing device.

15 13. A spintronic, a magnetic or magneto-sensing device comprising a material located in or on a reflective or photonic structure, said device being characterized in that said structure has an electromagnetic mode which is by design or can be made by way of adjustment or tuning, resonant with a transition in said material and in controlling, in particular enhancing, the magnetism in said material, by means of strongly coupling said material to the local electromagnetic vacuum field and exploiting the formation of extended macroscopic states in said material, namely states of spatial extension exceeding the size of the grains of said material.

20 25 14. A device according to claim 13, characterized in that the concerned transition is one of an electronic, a vibrational or a phonon transition.

30 15. A device according to claim 13, characterized in that the reflective or photonic structure comprises plasmonic structures, the electromagnetic mode being a surface plasmon mode.

16. A device according to claim 13 characterized in that the reflective or photonic structure consists of an optical microcavity, preferably a Fabry-Perot cavity, the electromagnetic mode being a cavity mode.

35 17. A device according to anyone of claims 13, 14 and 16, characterized in that the reflective structure comprises two metallic or dielectric mirrors forming with the material a sandwich structure, the distance

- 18 -

between said mirrors being adjusted to resonate with a transition in said material.

18. Machine or apparatus able and intended to perform at least one magnetic function, wherein said machine or apparatus comprises at least one device according to anyone of claims 13 to 17, said device being designed to perform the method according to anyone of claims 1 to 12.
- 5

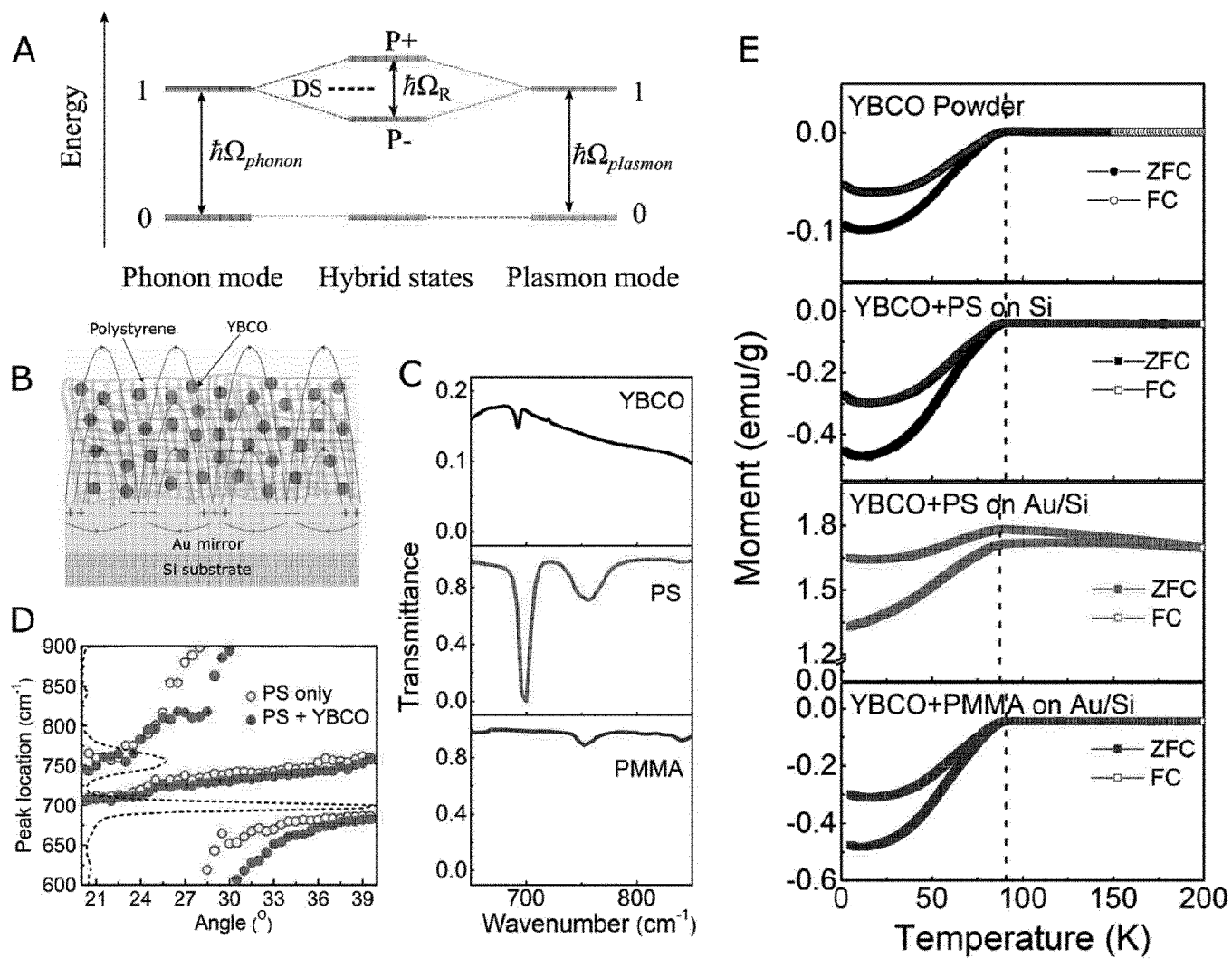


FIG. 1

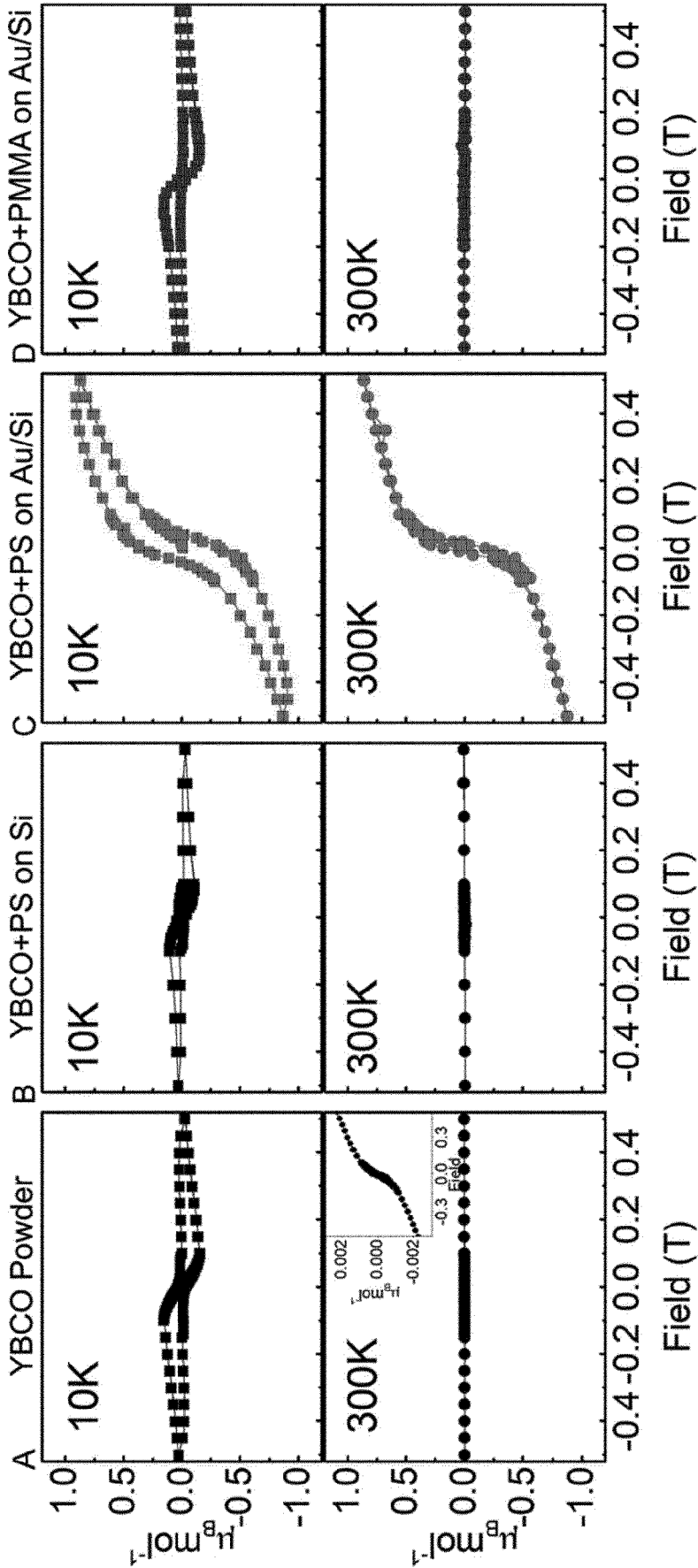


FIG. 2

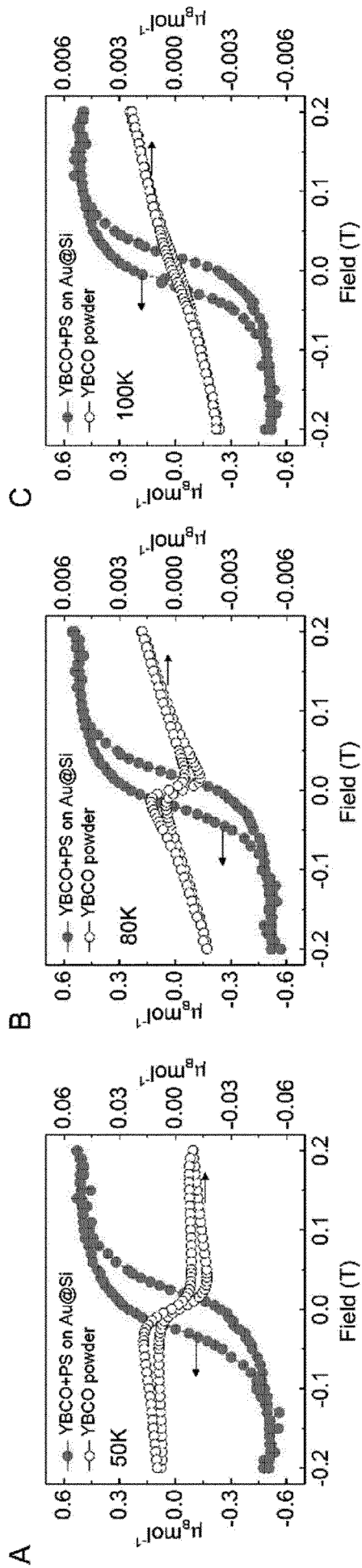
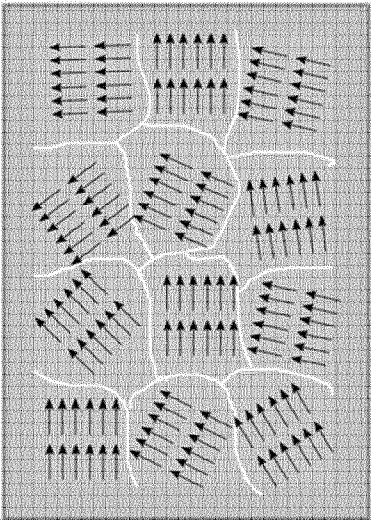
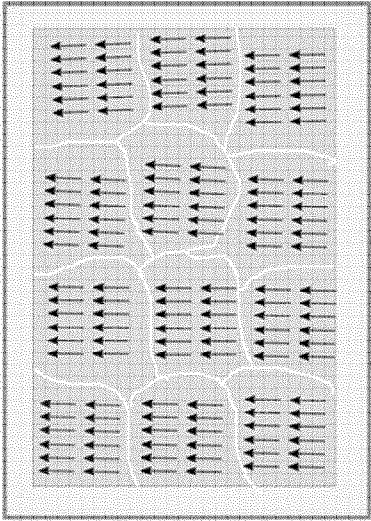


FIG. 3

B



Strong
coupling



A

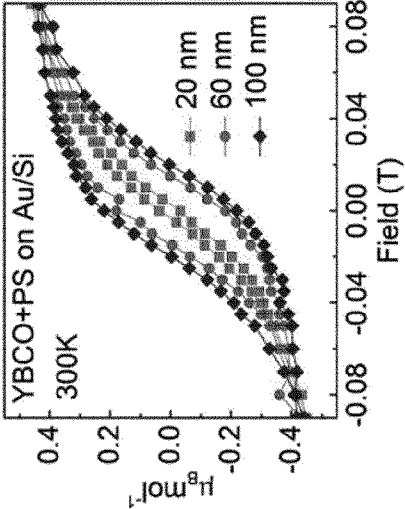


FIG. 4

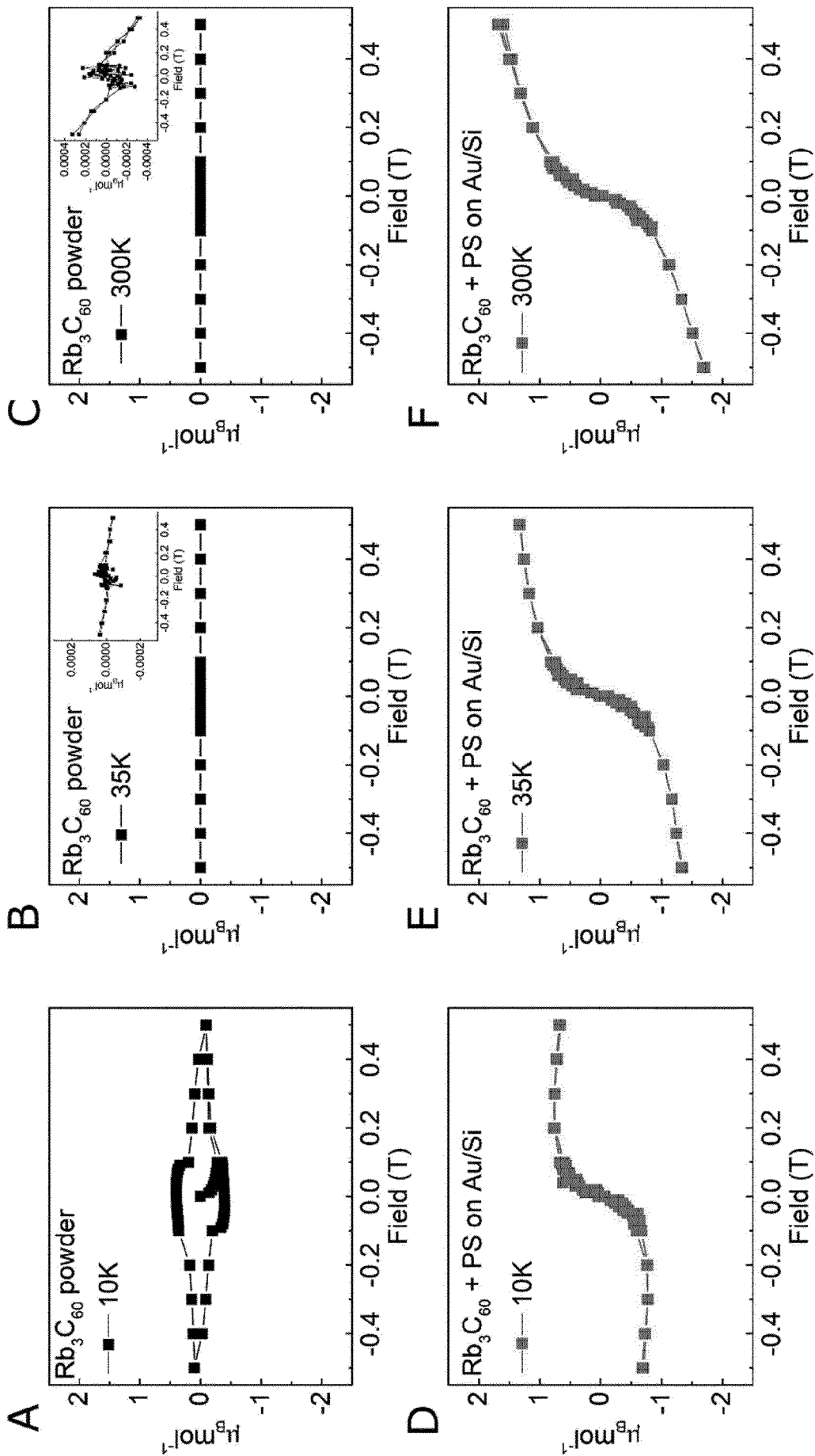


FIG. 5

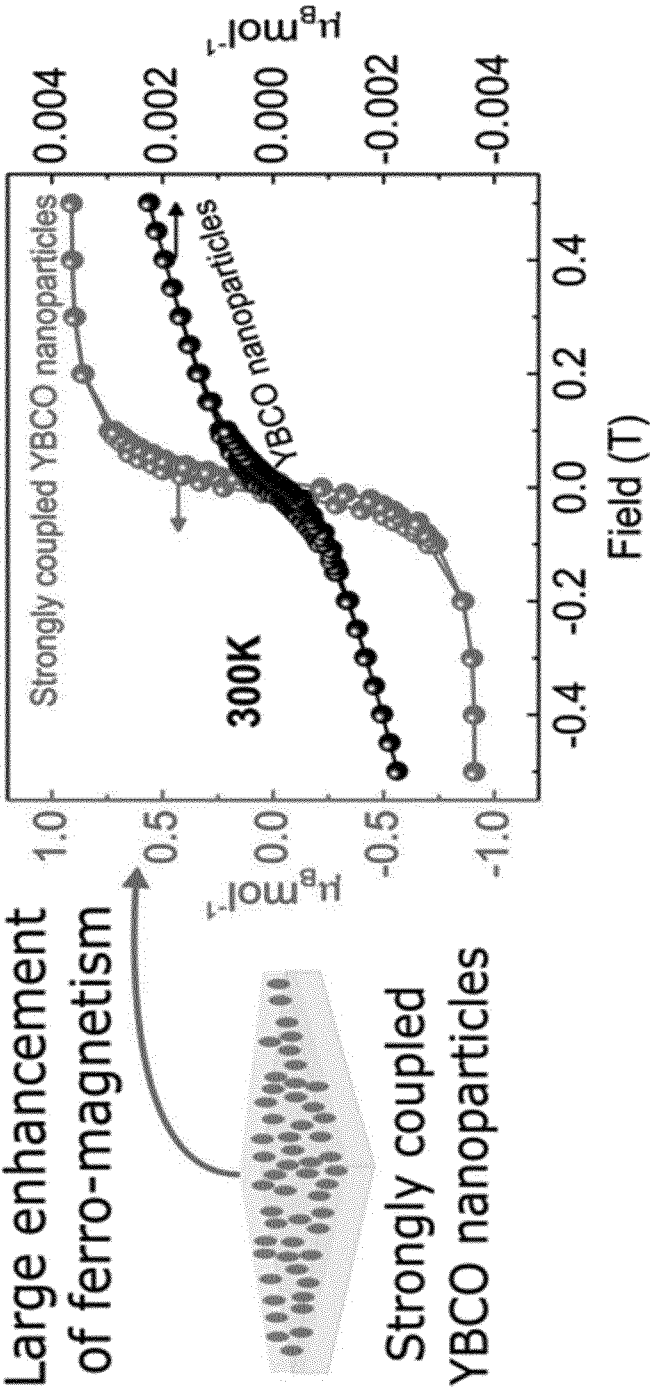


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/055510

A. CLASSIFICATION OF SUBJECT MATTER INV. G02F1/00 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) B82Y		
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 practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ANOOP THOMAS ET AL: "Exploring Superconductivity under Strong Coupling with the Vacuum Electromagnetic Field", ARXIV.ORG, CORNELL UNIVERSITY LIBRARY, 201 OLIN LIBRARY CORNELL UNIVERSITY ITHACA, NY 14853, 4 November 2019 (2019-11-04), XP081569123, cited in the application	1-3, 6, 8-15, 17, 18
Y	the whole document ----- -/--	4, 5, 7, 16
☒ 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 application or patent 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		Date of mailing of the international search report
21 June 2022		29/06/2022
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 Verbandt, Yves

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/055510

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SENTEF E R ET AL: "Cavity quantum-electrodynamical polaritonically enhanced electron-phonon coupling and its influence on superconductivity", SCIENCE ADVANCES, vol. 4, no. 11, 30 November 2018 (2018-11-30), pages 1-6, XP055933200, DOI: 10.1126/sciadv.aau6969 Retrieved from the Internet: URL:https://www.science.org/doi/10.1126/sciadv.aau6969> the whole document -----	4, 5, 16
Y	WANG KUIDONG ET AL: "Large optical nonlinearity enhancement under electronic strong coupling", NATURE COMMUNICATIONS, vol. 12, no. 1, 5 March 2021 (2021-03-05), XP055933574, DOI: 10.1038/s41467-021-21739-7 Retrieved from the Internet: URL:http://www.nature.com/articles/s41467-021-21739-7> the whole document -----	7
A	SHIN DONGBIN ET AL: "Phonon-driven spin-Floquet magneto-valleytronics in MoS2", NATURE COMMUNICATIONS, vol. 9, no. 1, 12 February 2018 (2018-02-12), XP055933203, DOI: 10.1038/s41467-018-02918-5 Retrieved from the Internet: URL:http://www.nature.com/articles/s41467-018-02918-5.pdf> -----	1-18
A	MACCAFERRI NICOLÒ ET AL: "Nanoscale magnetophotonics", JOURNAL OF APPLIED PHYSICS, AMERICAN INSTITUTE OF PHYSICS, 2 HUNTINGTON QUADRANGLE, MELVILLE, NY 11747, vol. 127, no. 8, 28 February 2020 (2020-02-28), XP012245008, ISSN: 0021-8979, DOI: 10.1063/1.5100826 [retrieved on 2020-02-28] ----- -/--	1-18

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/055510

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NAVARRETE BRAYAN ET AL: "Nanomagnetic Particle-Based Information Processing", IEEE TRANSACTIONS ON NANOTECHNOLOGY, vol. 18, 10 September 2019 (2019-09-10), pages 983-988, XP011748006, ISSN: 1536-125X, DOI: 10.1109/TNANO.2019.2939009 [retrieved on 2019-09-27] -----	1-18