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Magnetism : another idiosyncrasy of Boron ?

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This paper is dedicated to Dr. Jean-Paul Kappler.

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Abstract: We have studied the magnetic properties of various Boron particles obtained by different methods and have found evidence of soft ferromagnetism in all. While our study cannot unequivocally exclude that Boron is at the origin of the magnetism, we suggest that various impurities which are either the result of the synthetic process or come from the intentional doping of the Boron particles are indeed responsible for the observed magnetic properties. The phenomenon bears similarities with what is observed in magnetic oxides such as MgO or ZnO.

Introduction

Boron is a peculiar element. It is not a product of nucleosynthesis unlike most elements,^{1,2} it cannot exist in water as an ion,³ it is considered essential to life even though its role remains unclear,^{4,5} it possesses a great many allotropes.⁶ Boron and its derivatives have found countless uses throughout history, from the embalming of mummies to the doping of semi-conductors, through the fabrication of glassware and neutron shielding. There is even a city named Boron in California, the site being the world's largest source of borax. Not so many elements can boast being the eponym of a city. Boron is diamagnetic in its bulk form but is ubiquitous in the NdFeB magnets found nowadays in

smartphones, generators and hard drives.⁷ Calculations predict that 2-D boron, “borophene”, could become superconducting below 20K.^{8,9} Even though there are numerous studies reporting the influence of boron doping/alloying on the magnetic properties of a variety of materials,¹⁰ there seems to be very few dealing with the magnetic properties of pure Boron,^{11,12,13,14} in particular we failed to find a recent one or one dealing with nanoparticles.

We have examined the magnetic properties of four batches of particulate Boron: two commercial samples and two lab-made samples. Surprisingly, all samples displayed soft ferromagnetism at room temperature.

Results and Discussion

We synthesized (samples BL8 and BL14) and purchased (samples PVZ and HCS) Boron particles in order to prepare MgB₂ which is then subsequently used for the fabrication of superconducting wires and tapes. When used in this context, it has been shown that adding Carbon to the materials increases the upper critical field H_{c2} without losing too much on the critical temperature T_c . Carbon atoms and clusters are thought to act as pinning centers for the flux lines. The samples involved in this study therefore have a carbon content ranging from 0.8wt.% to 6.0wt.%. See Supplementary information (S1, S2, S3) for details on the synthesis, composition and other information.

We have performed SQUID magnetometry on the four different samples in powder form. Figure 1 displays the raw magnetization curves of all samples, at 300K. The central parts ("minor cycles") are shown in Figure 2 in order to give more details on remnant magnetization and coercive field. Depending on sample history the first magnetization curve is not always visible but since the samples are not magnetic in the traditional sense, i.e. with domains and walls, the first magnetization curves bear no particular significance.

Figure 1. Magnetization curves of the samples, at 300K. No correction for the diamagnetism of the sample holder or dotriacontane were applied (i.e. raw data)

The magnetic response at room temperature is essentially diamagnetic but soft ferromagnetism is obviously present, as can be clearly seen in the low-field region of the curves. A small remnant magnetization and a modest coercivity are visible for all samples. Boron electronic structure is $1s^2 2s^2 2p^1$, it is a semi-conductor with a bandgap ranging between ca. 0.60eV to 2.6eV, depending on the allotrope. It conducts electricity at high temperature but is insulating at low temperature. Not being a paramagnetic element and lacking conduction electrons, pure Boron cannot sustain regular para- or ferro-magnetism in its bulk form. It is therefore rather surprising to observe a deviation from diamagnetism. This being said, one has to observe that many other elements or materials seem to “become magnetic” when prepared in the form of nanoparticles (e.g. Au, Ag, Cu,...), we shall discuss this point more hereafter.

Figure 2. Hysteresis cycles of the samples at low fields, at 300K. No corrections for the diamagnetism of the sample holder or dotriacontane were applied (i.e. raw data). Depending on sample history the first magnetization curve is not always visible.

We have further characterized the samples by recording the behavior of the magnetization upon cooling and field-cooled / zero-field-cooled (FC/ZFC) magnetization curves. A representative example is given in figures S4 and S5, all samples displayed very similar behaviors.

For all samples, the curves are featureless, showing only a monotonous increase of the magnetic moment upon decreasing the temperature. The magnetic susceptibilities do not follow a proper Curie or Curie-Weiss law, as seen in figure S6, though some linearity can be found over limited portions of the temperature range. More, the ZFC curves do not have the characteristic form usually

observed with magnetic nanoparticles, there is no evidence at all of a blocking temperature. These measurements imply that the observed magnetism does not stem from para- or ferro-magnetic impurities. This is in contradiction with the measurements of reference 14 where the authors not only observe a monotonous non-saturating magnetic moment as a function of the applied field, and a susceptibility which follows a proper Curie law. Like ours their samples were carbon doped but, contrary to ours, they were crystalline. A final evidence that the magnetism is not brought by 3d elements is the absence of specific spectral lines in the energy-dispersive x-ray spectroscopy (EDX) spectra, as illustrated in figure S3 (though traces are detected).

Last, magnetization curves were recorded at 4K, they are given in figure S7. At this temperature the diamagnetic contribution becomes dominated by the para- and ferro-magnetic components. Ferromagnetism remains soft, the curves looking very much like paramagnetism Brillouin curves and the opening of the hysteresis cycles being quite modest.

The coercive fields and remnant magnetizations are summarized in Table 1. For all samples the remnant magnetization is equal or larger at low temperature. The behavior of the coercive fields is more puzzling. The coercive field of sample PVZ is larger at 4K –as usually observed in magnetic materials– but samples BL8, BL14 and HCS all display a surprising increase of their coercive field with temperature. We are tempted to ascribe this to an increased number of electrons in the conduction band when the temperature is risen.

Table 1. Remnant magnetization and coercive field of all samples.

	T = 300K		T = 4K	
	Remnant magnet. (emu/gram)	Coercive field (G)	Remnant magnet. (emu/gram)	Coercive field (G)
BL8	3.5×10^{-4}	1000	3.4×10^{-4}	42
BL14	7.9×10^{-4}	700	1.8×10^{-3}	75
PVZ	7.3×10^{-6}	350	1.1×10^{-3}	1030
HCS	1.6×10^{-4}	320	1.9×10^{-4}	28

Even though ubiquitous in modern days as part of NdFeB magnets, Boron is not a material commonly encountered in magnetism. There have been many studies devoted to borides but boron itself has not been much investigated. This is probably due to the facts that it is still difficult to prepare reasonably pure Boron samples and that there are at least 14 known allotropes for crystalline Boron, each with a peculiar electronic structure. A glimpse on the complexity of Boron physical properties can be obtained in the book edited by V.I. Matkovich.¹⁵ A paramagnetic susceptibility has been observed in amorphous Boron above room temperature and been ascribed to thermal excitation of localized centres.¹² Crystalline β -rhombohedral Boron has been found diamagnetic below room temperature by Matyáš.¹¹ Tsiskarishvili et al. observed a paramagnetic ESR signal between 100 and 450K, which they ascribe to the presence of holes captured on trapping levels.¹³

Magnetic materials usually comprise 3d and/or 4f metals such as Fe, Ni, Co, Sm, Gd, etc. but more original magnetic alloys exist which do not make use of paramagnetic elements, such as TiBe₂ or ZrZn₂. Nanoparticles of Au, Ag, Cu have also been found to deviate from the diamagnetic nature of the elements bulk form,^{16,17} with the origin of the magnetism still being debated. Beyond systems which are metallic and made from paramagnetic elements, magnetism in materials can also arise from a variety of reasons which could be dubbed as extrinsic. Room-temperature ex nihilo

ferromagnetism has been observed in CdSe nanoparticles¹⁸ and attributed to the formation of holes in the material due to the electron transfer caused by the bonding to the capping ligands. Magnetic moments were of the order of a few 10-2emu/gram at room temperature and coercive fields lay around ~100G between room temperature and 4K. A similar observation has been reported for ZnO nanoparticles, with the same explanation put forth.¹⁹ Moments are weaker by at least one order of magnitude, with no or a very small opening of the hysteresis cycle. All these materials are semiconductors. Pure sodium chloride NaCl, which is ionic and insulating, has also been found to display some ferromagnetism at room temperature, the explanation offered being that surface Cl deficiencies bear a magnetic moment and neighboring vacancies couple ferromagnetically.²⁰ Along this line, since massive Boron is insulating and diamagnetic it seems reasonable to correlate the appearance of magnetism with either a surface effect or the size effect which occurs for most materials when prepared in nanoparticle form. Regarding the latter, suffice it to look at the original optical properties displayed by semiconductors such as CdTe or PbSe when they form so-called “quantum dots”. Still, given the rather large size of our Boron particles, more micro than nano, this size effect is probably not at the origin of the observed magnetism. (Figure S1 gives representative SEM images of the samples.)

Three samples, BL8, BL14 and HCS have a rather ill-defined morphology, with jagged particles, looking like ground glass. On the contrary sample PVZ turns out to be much more regular, with rather spherical particles, even if the size dispersion looks rather large. Interestingly, this sample has the second highest Boron content (94.2%) and it also displays the most ferromagnetic-like curves, even if its remnant magnetization is the lowest. Its coercive field reaches a value of 1000Oe at 4K. We find it tempting to correlate the reinforcement of magnetism (in the sense of more ferromagnetic-like) to the regular morphology of the particles and the better purity.

Given the nature, size and morphology of the particles we envision two possible origins for the magnetism: giant orbital paramagnetism or oxygen vacancies, both relevant in the presence of bandgaps.

Giant orbital paramagnetism, a peculiar form of magnetism not based on interacting spins, also called “d-zero magnetism” by J.M.D. Coey has been invoked to explain the magnetic properties of porous alumina.^{21,22} It originates in the influence of zero-point fluctuations of the vacuum electromagnetic field on bound electrons which stabilizes a collective ground-state energy, leading to novel effects such as ferromagnetism at room temperature for quasi-two-dimensional systems. Still, being field-induced, it is not a rigorous ferromagnetism. The effect is most likely to be observed at the surface of materials with low electron density and high dielectric constant.²³ The coherent orbital character of the dilute electronic assembly is almost temperature independent since it is a ground state. While it is difficult to totally rule out the possibility that some giant orbital paramagnetism be present, our results are nevertheless at odds with the findings of Coey since, contrary to his, our magnetization curves at 4K and 300K do not superimpose.²⁴

Let us now consider the other possibility, defects and vacancies. Oxygen and Carbon are present in all our samples so some oxides and/or carbides are possibly present. Defects and vacancies can give rise to some magnetism, as it has been observed for e.g. Cerium oxide. ²⁵ If F⁻ centers (oxygen defects with two trapped electrons) and F⁺ centers (oxygen defects with one trapped electron) are indeed present in significant amounts, the samples should exhibit some luminescence in the visible spectrum. We could not detect luminescence in the samples examined with a sensitive spectro-fluorimeter.

F-centers usually are paramagnetic. A simple test is to perform electron spin resonance (ESR) measurements. As for the luminescence, all samples exhibit an ESR signal, as seen in figure 3. Signals are actually quite strong. We cannot, of course, unequivocally assign the ESR response to the sole F-centers.

Interestingly, each sample has a specific lineshape. While HCS and PVZ sample exhibit lines which could be described as “simple”, BL8 and BL14 possess more complex ones. BL8 has a rather broad lineshape, BL14 clearly displays two superimposed responses. A broad lineshape usually implies that some magnetic coupling between sites is present. It is therefore surprising that HCS and BL8 samples have quite different lineshapes when their magnetic behaviour is quite similar (see figs. 2 and S7). Sample PVZ, which is close to displaying a ferromagnetic behaviour, also has a simple narrow ESR lineshape. A tentative deconvolution of the ESR lineshapes is given in figure S8.

Figure 3. Room temperature experimental EPR spectra (black line) of BL8, BL14, PVZ and HCS Boron nanoparticles, together with respective simulations attempts (red line) (see SI for details on spectral deconvolution).

Magnetically ordered clusters of electron spins localized at oxygen vacancies would be expected to behave super-paramagnetically whereas our FC-ZFC curves do not evidence any blocking temperature. It is therefore not clear why some measurements would imply a certain amount of coupling between magnetic centers whereas other would not.

In one ESR study on amorphous Boron, Tsiskarishvili et al.¹³ report an ESR study of amorphous Boron. Just like ours, their samples had a noticeable amount of Oxygen (2%) and Carbon (figure not given). They observe in particular an ESR signal comprising two components having nearly the same g factor. No picture of the lineshape is provided nor the values of g but one could probably find similarities with our lineshapes, especially that of sample BL14. Their conclusion is that the

magnetism is intrinsic and results from holes trapped on very shallow trapping levels just above the valence band. In another study¹⁴ on crystalline β -Boron they report that two ESR signals having $g=2.00$ and $g=4.28$ were observed, the latter being ascribed to Fe^{3+} impurities. We did not observe a signal corresponding to $g=4.28$. The role of Carbon doping is unclear but it is suggested that Carbon atoms could act as donors substituting Boron atoms in the lattice,¹⁴ even though no clear dependence between the magnetism and the Carbon content could be found.

The question of how magnetic centers diluted in an insulating or a large bandgap material can become coupled is not a simple one. Given the weakness of the moments and the average distance between them, dipolar coupling can most certainly be ruled out. Direct or indirect magnetic coupling mechanisms (i.e. electron mediated) between magnetic moments are not at all evident for the stabilization of the long-range ferromagnetic order since Boron is insulating. Ferromagnetism in insulators has already been observed in materials such as MgO ,²² ZnO ²⁶ or HfO_2 ,²⁷ to name but a few. In these undoped materials, the magnetic centers are generally vacancies of the metallic element. The ferromagnetic coupling between magnetic centers is then mediated by the 2p orbitals of oxygen. In the case of Boron, which is 2p¹, such a coupling can probably be ruled out. The only possibility left is that impurities create a conduction band within the Boron bandgap. The question of impurities conduction band is well known²⁸ and, for example, doping the aforementioned oxides with metals or other impurities such as N or C is known to create localized energy bands that can then either sustain carriers mobility or facilitate the coupling with the host conduction band.²⁹ We therefore propose that a similar process is at work in the Boron particles, with either Mg, O or C acting as impurities, simultaneously creating magnetic centers and enabling their ferromagnetic coupling.

Conclusion

We have studied the magnetic properties of Boron particles and observed soft ferromagnetism from 4K up to 300K. Samples synthesized in different places with different methods all exhibit similar behaviors. We suggest that the magnetism does not originate on Boron itself but is related to impurities and dopants which are present in the material while in the same time a surface effect could also play a role in the magnetic behavior.

Experimental Section

Materials and methods

Boron particles synthesis : The PVZ nanoB (98.5 wt.% in purity) sample, produced by diborane thermal decomposition, was purchased from Pavezyum Kimya, Advanced Chemicals, Istanbul – Turkey.³⁰ The HCS micrometric B powder (grade I: min. 95 wt. % in purity), prepared by magnesiothermal reduction, was acquired from H. C. Starck GmbH.³¹ Instead, BL8 and BL14 were prepared at CNR-SPIN lab of Genoa (Italy) following the European Patent described in references 32, 33, 34. Briefly, the B nanostructuration process can be summarized as follows. In order to obtain pure nanoB, B_2O_3 ($\geq 98\%$ in purity, purchased from Sigma-Aldrich, now Merck) was solubilized in hot deionized water and then atomized into liquid nitrogen (LN_2). The solid phase ($\text{H}_2\text{O}-\text{B}_2\text{O}_3$) was freeze-dried to sublimate water and the so-obtained nano B_2O_3 was reduced to elemental nanoB following the magnesiothermal reaction of the Moissan's Process. The same procedure was adopted to prepare BL14, in this case a nominal 6 wt. % hemoglobin was dissolved in H_2O together the B_2O_3 , more and newer details are provided in reference 35, in particular from superconducting point of view.

Electron Paramagnetic Resonance (EPR) investigations: Continuous-wave EPR investigations were performed at room temperature using EMXplus X-band spectrometer (Bruker Biospin GmbH, Germany) equipped with a high-sensitivity resonator (4119HS-W1, Bruker). This setup was used to record conventional field-swept spectra of each powder of nanoparticles (ca. 50 mg) introduced into 4 mm outer diameter quartz tubes (Wilma-Labglass). The principal experimental parameters values were a modulation amplitude of 2G, a microwave power of ca. 1.8 mW, a time constant of ca. 40 ms and a conversion time of ca. 150 ms. The g factor was calibrated using Bruker strong pitch standard of known g factor 2.0028.

SQUID magnetometry : Magnetometry has been performed with a Quantum Design MPMS3 magnetometer. The nanoparticles were simply hand-pressed into a standard gelatin container and pure molten dotriacontane wax was poured on top in order to mechanically stabilize the powder. Both gelatin container and dotriacontane were previously magnetically tested in the SQUID and returned only a weak diamagnetic signal ($\chi_{dia} \sim -1.3 \times 10^{-4} \text{emu.g}^{-1}$). As subtracting this diamagnetic contribution did not change much the shape of the curves nor did it affect the discussion, we have chosen not to remove it from our data.

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Supplementary information

Figure S1 - Electron microscopy :

Figure S1. Scanning electron micrographies of the four samples at comparable magnifications.

Table S2 - Elemental composition :

By recording EDX spectra we have checked that no ferromagnetic impurities were present, at least to our detection level. The magnitude of the magnetic moments that we measure would imply that any impurity such as Fe or Mn would clearly show up in the EDX analysis.

Sample	Diameter (nm)	B content in (wt. %)	C content in (wt. %)	Mg content (wt. %)	O content in (wt. %)	SUM
BL8	280	90.8	0.0	7.3	1.9	100
BL14	110	80.7	4.5	5.3	9.5	100
PVZ	<250	97.5	0.0	0.0	2.5	100
HCS	<1	98.2	0.0	0.2	1.6	100

Table S2. Physico-chemical properties of the samples.