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Defect-Induced Magnetism in Solids

(Invited Paper)

Pablo Esquinazi[1], Wolfram Hergert[2], Daniel Spemann[1], Annette Setzer[1], and Arthur Ernst[3]

[1]Institute for Experimental Physics II, Fakultät für Physik und Geowissenschaften, University of Leipzig, 04103 Leipzig, Germany
[2]Institute of Physics, Martin Luther University Halle-Wittenberg, 06120 Halle, Germany
[3] Max Planck Institute of Microstructure Physics, 06120 Halle, Germany

In the last years the number of nominally non-magnetic solids showing magnetic order induced by some kind of defects has increased continuously. From the single element material graphite to several covalently bonded non-magnetic compounds, the influence of defects like vacancies and/or non-magnetic ad-atoms on triggering magnetic order has attracted the interest of experimentalists and theoreticians. We review and discuss the main theoretical approach as well as recently obtained experimental evidence based on different experimental methods that supports the existence of defect-induced magnetism (DIM) in non-magnetic as well as in magnetic materials.

***Index Terms*—oxides, graphite, defects, impurities**

I. Why Defect-Induced Magnetism was recognized so late?

In the original publication of Heisenberg, published in Leipzig in 1928 [1], about the basic concepts on the origin of magnetic order in solids, it is written at the end of the paper that the principal quantum number of the electrons responsible for the magnetism must be $n \gtrsim 3$. It took several decades till scientists started thinking that magnetic order may exist beyond this $n \gtrsim 3$ condition. The reason why magnetism based on s and p electrons was finally predicted, discovered and recognized so late, is mainly due to a mixture of three things, namely: The first reason is theoretical, since Heisenberg's successful theory on magnetic order promoted a kind of magnetic prejudice against magnetic signals coming from compounds with full d- or f-bands or materials with only s and p electrons. Second, the contribution of magnetic impurities and their usually difficult characterization put also hard constraints, which till now are not always removed. Finally, the phenomenon of defect-induced magnetism (DIM) in systems without usual magnetic ions is based on the effect of different kinds of defects upon the system. The production of samples with a homogeneous distribution of defects at the right lattice positions remains difficult. Therefore, the obtained magnetic signals are in some cases so small, that even tens of ppm of magnetic Fe would be enough to produce similar ones. Thus, the answer to the question of this section is a mixture of technical capabilities to check for the impurity contribution, scientific (over)skepticism and the nature of the DIM phenomenon itself.

In spite of these "difficulties", the DIM phenomenon has been finally observed in a broad spectrum of materials, from carbon-based to several oxides and the obtained evidence of the last ten years leaves little doubt about its existence. In this contribution we do not try to review the huge amount of studies published but we would like to emphasize a few new theoretical and experimental results from different groups as well as from us obtained in the last years that we believe should be of interest for all scientists working on this subject.

Corresponding author: P. Esquinazi (email: esquin@physik.uni-leipzig.de).

II. Basic ideas and general theoretical approach to the problem

In parallel to the experimental exploration of the unusual magnetism, not based on d or f electrons, theoretical studies emerged. Theoretical investigations can be based on model Hamiltonians to study basic physical features of the problem [2], [3]. Detailed considerations of native defects, hydrogen or light impurities in carbon or oxides require calculations on the *ab initio* level, based on density functional theory (DFT). The application of sophisticated computer codes is not without problems and the complete discussion of DIM demands a multicode approach.

An intensive search for new routes to ferromagnetic oxidic materials started with the investigation of Elfimov *et al.* [4]. Using CaO as an example, it was demonstrated that dilute divalent cation vacancies in oxides with rocksalt structure lead to a ferromagnetic ground state. The quite general result in [4] that the spin triplet state is the ground state, is also applicable to other compounds with vacancies in octahedral coordination. In terms of this somehow initiating paper an innumerable series of papers appeared during the last 10 years investigating the electronic and magnetic properties of vacancies and non-magnetic impurities in different oxides, whereas especially MgO and ZnO attracted the attention [5]–[7].

A consistent theoretical proof of a stable ferromagnetic ground state consists of several steps. First, one has to calculate the magnetic properties of the corresponding vacancies and impurities in the dilute limit. Second, the mechanism of magnetic interaction as a requirement of long-range magnetic order has to be investigated. Third, a calculation of the transition temperature has to predict the temperature range of ferromagnetic order. All steps are connected with problems, as discussed by Zunger *et al.* [8]. Those problems and the restricted knowledge of the nature and distribution of defects

in experimental investigations, usually used as input of calculations, limit the predictive power of *ab initio* calculations.

As a result of DFT calculations cation vacancies in ZnO carry a magnetic moment of $1.89\mu_B$ [9]. The magnetic interaction of such defects breaks down if localization corrections [8] are taken into account. Calculations on Open-shell impurity molecules like C_2 in ZnO seem to be a possible way for long-range ferromagnetic order in ZnO as calculations demonstrated [5].

Surfaces provide another route to controlled ferromagnetism in an otherwise non-magnetic host material. We studied room-temperature p-induced surface ferromagnetism at the oxygen-terminated ZnO(001) surface [10]. The pseudopotential code SIESTA was used to relax the structure. For a more adequate description of the correlated electrons a multiple scattering Korringa-Kohn-Rostoker code [11] was used. The code provides the real space exchange coupling constants, which serve as an input to a Monte Carlo simulation in the framework of a classical Heisenberg model to determine the Curie temperature. Finally it was shown, that the surface is thermodynamically stable and ferromagnetic at room temperature [10].

III. DIM IN CARBON

Already in 1968 the possibility to have magnetic order in hypothetical hydrocarbons was emphasized by Mataga in a short paper [12]. Within the same line, in 1974 Tyutyulkov and Bangov proposed theoretically the existence of unpaired electrons in hydrocarbon molecules and nonclassical π-conjugated polymers [13]. Ovchinnikov and coworkers followed a similar line [14], [15] and in 1991 they proposed a pure carbon structure based on 50% graphite and 50% diamond bondings that could show magnetic order with a saturation magnetization above 200 emu/g [16], comparable to α-Fe. Although this structure apparently was not reproduced or realized, later experiments with disordered or amorphous carbon obtained by pyrolysis of certain precursors indicated the existence of magnetic order with critical temperature above 500 K and saturation magnetization $\sim$ 10 emu/g at 4.3 K [17]. Further details of this early work can be seen in [18]. The main problem of the early work is the unclear contribution of magnetic impurities, basically due to insufficient characterization of their density and reproducibility of the reported phenomenon. In this section we discuss results related to the magnetic order mainly found and confirmed in graphite samples. Recent experimental studies did not provide clear evidence for the existence of this phenomenon in single layer graphene [19], [20] and therefore we will not discuss them here due to the available space. The importance of the 3D lattice structure of graphite to trigger magnetic order through carbon vacancies or bonded hydrogen has been emphasized in [21], see also [3].

A. DIM in as-received graphite samples and the contribution of magnetic impurities: A never end story

The relatively small ferromagnetic moments obtained in most of the materials that show DIM due to the actually "brute force" production methods used to trigger this phenomenon, make the knowledge of the ferromagnetic contribution from

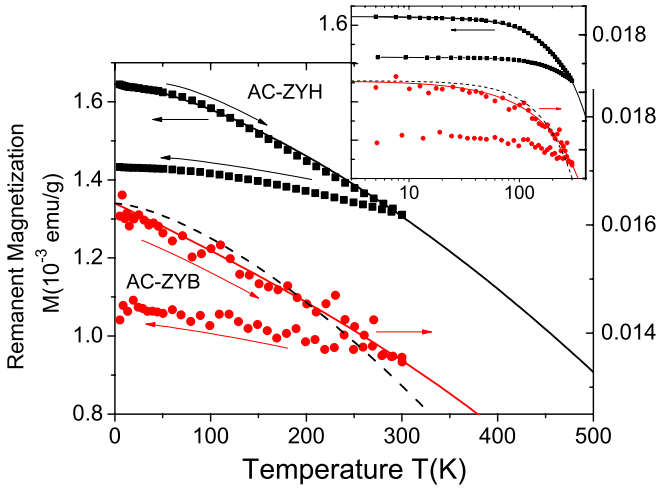

Fig. 1. Remanent magnetization at zero field measured after field cooling the samples in a field of 1 T to 5 K. The data have been taken by warming to 300 K and cooling down to 5 K, see arrows. The results of two HOPG samples are shown: AC-ZYH (upper black data points) and AC-ZYB (lower red data points). The inset shows the same data but in a semi logarithmic scale. The continuous black top line was calculated using the 3D Bloch $T^{3/2}$ model with the following parameters: Curie temperature $T_c = 800$ K, a ratio $2JS/k_B = 210$ K (J the exchange coupling and S the total spin). For the AC-ZYB sample the remanence follows an anisotropic 2D spin waves model, continuous red line [22], [23], which follows a nearly linear decrease of the magnetization with temperature. The continuous line was calculated using the following parameters: Critical temperature $T_c = 600$ K, spin-wave critical temperature due to low-energy spin-wave excitations $T_c^{SW} = 1950$ K and anisotropy $\Delta = 0.001$. For comparison we show the theoretical (dashed) line obtained within the 3D Bloch $T^{3/2}$ model with the best parameters set to fit the data of sample AC-ZYB.

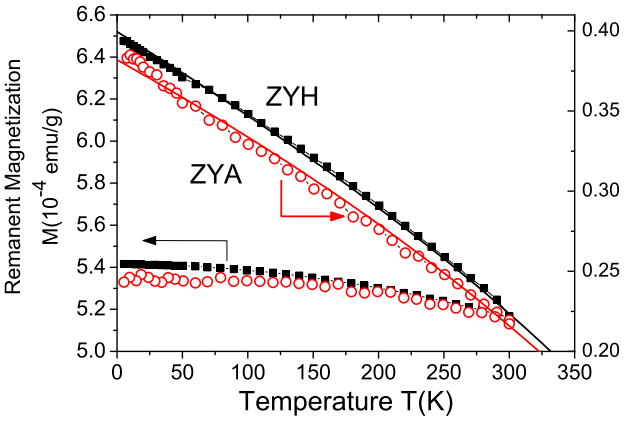

Fig. 2. Temperature dependence of the remanent magnetization, similar as in Fig. 1, for two HOPG samples after field cooling the samples in a field of 1 T to 5 K. The continuous lines follow the 2D Heisenberg model with anisotropy [22], [23] and were obtained with the following parameters for sample ZYH (ZYA): Critical temperature $T_c = 550$ K (750 K), spin-wave critical temperature due to low-energy spin-wave excitations $T_c^{SW} = 1700$ K (830 K) and anisotropy $\Delta = 0.001$.

magnetic impurities unavoidable to assure that the measured phenomenon is intrinsic. In this section we discuss mainly the magnetic contribution of impurities in the as-received state of the samples. Whatever is the as-received state of the sample to be characterized, one should not forget that ultrasonic cleaning is nevertheless required to get rid of the edge contamination graphite samples may have. The influence of defects or ion irradiation to the magnetism of graphite will be discussed in the next section.

There are basically two main problems to characterize the magnetic response from impurities using only the SQUID magnetometers. Firstly, the measurement of their concentrations. For concentration below 50 ppm there are not too many experimental methods able to measure this content with enough certainty. Second, the knowledge of their concentration alone is not enough. One needs to know at least the typical size of the impurity grains inside the material of interest, which requires a method for elemental imaging that provides excellent detection limits in the ppm and sub-ppm range together with reliable quantification, preferably in a non-destructive way. The sole measurement of the magnetic moment of a sample with a known amount of impurities does not provide always with a clear statement whether the ferromagnetism is or is not due to impurities. In this section we provide a simple example of this problem using the magnetization data of four as-received HOPG samples of different origins and impurity concentrations. A complete description of all measurements done in as-received HOPG samples including the elemental analysis as a function of position inside the samples using particle induced x-ray emission (PIXE, see for example [24]) will be published elsewhere.

Figure 1 shows the temperature hysteresis of the remanent (zero field) magnetization after cooling the samples in a field of 1 T, as a function of temperature of two HOPG samples with Fe concentration (the main magnetic impurity) 23 μg/g ($\simeq$ 5.8 ppm) for sample AC-ZYH and 0.2 μg/g ($\simeq$ 0.05 ppm) for sample AC-ZYB, within a relative error $\lesssim$ 10%. As shown in [24] the Fe is mainly distributed in spot-like regions of diameters $\lesssim$ 10 μm all over the sample interior (penetration depth of the PIXE analysis $\gtrsim$ 30 μm). For the sample AC-ZYH one recognizes a larger density of Fe atoms in the spots than in the spots of sample AC-ZYB, both samples appear to have similar density of spots. Therefore, the difference in Fe concentration of a factor 115 between the two samples is probably due to the difference in Fe concentration within the spots and also a bit due to spot size, because the spots (grains) appear larger for the AC-ZYH sample. Both samples show the typical field hysteresis with a ratio between saturation values at 5 K of M_s(AC-ZYH)/M(AC-ZYB)$\simeq 6\times10^{-3}/4\times10^{-5}=150$ (both values in emu/g). If *all* Fe would be ferromagnetic, from the ratio in concentration we would conclude that the Fe concentration roughly explains the difference in magnetization at saturation values as well as the ratio of 102 in the remanent magnetization, see Fig. 1. Taking into account that 1 μg/g of ferromagnetic Fe (Fe_3O_4) in graphite would produce a magnetization at saturation of 2.2×10^{-4} emu/g (1.4×10^{-4} emu/g), if *all* the measured Fe concentration would be ferromagnetic we would have the magnetization values at saturation of 5×10^{-3} emu/g (3.2×10^{-3} emu/g) for sample AC-ZYH and 4.4×10^{-5} emu/g (2.8×10^{-5} emu/g) for sample AC-ZYB. From these estimated values it appears that all the measured Fe, if ferromagnetic, would be enough to explain the observations. It should be noted, however, that Fe in general is not homogeneously distributed in the micron-sized impurity grains as revealed by PIXE elemental imaging. For example, the main impurity contamination in these grains in AC-ZYB is Ti and V, but in AC-ZYH the Fe and V concentrations are similar whereas the Ti contamination can be neglected. Consequently, the impurity grains in both samples are different and cannot be considered to be of pure Fe (or Fe_3O_4).

Furthermore, Fe in graphite not always shows a ferromagnetic behavior or induces one, upon grain size and distribution. For example, in [25] a sample with an inhomogeneous Fe concentration of up to 0.38% (in weight) shows no magnetic order at all. Moreover, no increase in the magnetic order, existing in the as-received state, was measured in HOPG samples after implanting Fe up to concentrations of 4000 μg/g [26]. In this last case, the obtained result appears reasonable because after implantation the Fe atoms reside as single atoms randomly distributed in the (disordered) graphite lattice. The $T-$dependence of the remanent magnetization suggests that not only Fe ferromagnetism is at work in the as-received samples. As shown in [24], to compare quantitatively the T-dependence of the ferromagnetic signal with appropriate models avoiding arbitrary background subtractions, we take the remanent magnetization measured at zero applied field. The observed hysteresis between warming and cooling, see Fig. 1, is a clear evidence for the existence of a ferromagnetic state with Curie temperature above 300 K.

For large enough 3D ferromagnetic Fe particles we expect to see a $T-$dependence of the remanent magnetization given by the excitation of spin waves following the usual 3D Bloch $T^{3/2}$ model [27]. The sample with the largest Fe concentration (AC-ZYH) shows a $T-$dependence for the remanent magnetization compatible with this law, see Fig. 1. However, for the other sample with 0.05 ppm Fe concentration, the $T-$dependence deviates from this law but decreases quasi-linearly with T, the same dependence observed for the magnetization of irradiated HOPG samples and interpreted in terms of 2D Heisenberg model with a weak anisotropy [28], [29], see Fig. 1. We may conclude that for the sample with the smaller Fe concentration a non-negligible part of the observed magnetic order comes from defects that induce a two dimensional anisotropic magnetism and is not due to ferromagnetic Fe or other magnetic impurities.

To check the above correlation we did similar measurements in two other samples of different origin. Figure 2 shows the results for the samples ZYH and ZYA with Fe concentrations (main impurity): 10.2 μg/g and 0.55 μg/g. The ratio between magnetizations at saturation at 5 K is M_s(ZYH)/M_s(ZYA)$\simeq 2.3\times10^{-3}/2.8\times10^{-4}=8.2$ (values in emu/g). This ratio does not follow the expected ratio (19) if *all* Fe would contribute to the ferromagnetic signal. Whereas M_s(ZYH) appears to be compatible assuming that *all* Fe concentration would contribute ferromagnetically, M_s(ZYA)

is a factor of 2.3 larger than the highest expected saturation magnetization. From this we conclude that an extra contribution produces the observed magnetic order. Interestingly, both samples show a quasi-linear temperature dependence for the remanence magnetization, see Fig. 2, which can be well fitted within the 2D Heisenberg anisotropic model. From all these studies we may conclude that extra contributions, other than those from magnetic impurities, to the observed ferromagnetic magnetization response exist in as-received graphite samples. No general answer can be given, however, even knowing the magnetic impurity concentration, to the question whether magnetic impurities are or are not the reason for the observed magnetic response in a given sample. For samples with a relatively large amount of magnetic impurities [30] it has little sense to speculate whether the DIM phenomenon can be clearly observed from the measurements.

B. The role of vacancies and hydrogen

The existence of DIM in graphite, as-received samples of different magnetic impurity contents [25], [31] as well as after inducing defects by ion irradiation [32], was later confirmed by independently done studies [3], [29], [33]–[40]. The main idea to interpret the existence of magnetic order in graphite [21], [41], [42] (for reviews see [3], [43]) is based in the long range interaction that appears between the nearly localized magnetic moments existing at carbon vacancies [44], [45], or when a proton is bonded to a carbon p-electron normal to the graphene layer [46]. That single vacancies in graphite can trigger a magnetic moment has been proved experimentally by STM spectroscopy [37] at the surface of a bulk graphite sample as well as by SQUID measurements of bulk samples irradiated with different ions and doses [38]. As expected, magnetic order was found only in samples in which a vacancy density of several percents was achieved, i.e. a distance between them of the order of 2 nm [38]. This density is necessary to get magnetic order in solids, independently of the details of the structure or elements that are in the lattice, provided that the vacancies or other defects in the lattice lead to nearly localized magnetic moments. Further recent studies on the magnetic order in graphite triggered by proton and helium irradiation were done in [47]; the observed magnetic order appeared to be linked to defects in the graphite planes, like vacancies. Electron spin resonance studies on proton-irradiated HOPG samples at different fluences indicated the existence of metalliclike islands surrounded by insulatinglike magnetic regions [48] in agreement with previous findings [49].

The intrinsic origin of the magnetic order triggered by proton irradiation on graphite has been backed by transmission x-ray magnetic circular dichroism (XMCD) studies [33]. That study left no doubt that carbon can be magnetic without the need of magnetic impurities. Further XMCD studies in as-received as well as in proton irradiated HOPG samples [36] showed that not only the carbon π-band is spin polarized but hydrogen-mediated electronic states also exhibit a net spin polarization with significant magnetic remanence at room temperature [36]. The obtained results showed that the magnetic signals originated mostly from a ~ 10 nm near-surface region of the sample, where the saturation magnetization may reach up to 25% of that of Ni. The results also indicated that hydrogen plays a role in the magnetic order but it is not implanted by the irradiation but should come from dissociation of H_2 molecules at the near surface region of the HOPG sample [36]. These XMCD results support the findings from a low-energy muon spin rotation experiment on HOPG samples that indicated the existence of a ferromagnetic surface of ~ 15 nm thickness [50]. Further theoretical work showed that the magnetic coupling becomes weaker when the hydrogen-hydrogen distance increases [41], [51].

According to [46] hydrogen absorption on a graphene sheet as well as hydrogen chemisorption in graphite [21], may lead to the formation of a spin-polarized band at the Fermi level and robust ferromagnetic order should appear. These theoretical studies are supported by the XMCD results referred above [36] and emphasize the need for further studies on the role of hydrogen in the magnetism of graphite. Searching for a simple method to trigger magnetic order in graphite samples of mesoscopic size through hydrogen doping, the authors in [52] treated graphite surfaces with sulfuric acid. It is known that this kind of acid treatment leads to hydrogen doping in the graphite structure. Indeed, the magnetization measurements of micrometer small graphite grains treated with sulphuric acid showed clear signs for magnetic order, which amount depends on the used dilution of the acid as well as on the treatment time; it decreased after mild annealing in vacuum [52]. Further evidence for the existence of magnetic order triggered by the acid treatment came from the anisotropic magnetoresistance (AMR), defined as the dependence of the resistance on the angle between the direction of the electric current and the magnetic field, both applied parallel to the main area of the sample [52]. The reported results indicated that the $L - S$ coupling in graphite is not negligible when a magnetic moment is originated by hydrogen doping (or due to vacancies). The observed rather large AMR values support a hydrogen-mediated magnetism in graphite in agreement with the XMCD results of [36].

IV. Evidence for DIM in Oxides

Nearly simultaneously with reports on magnetic order in graphite about 12 years ago, the search for ferromagnetism in diluted magnetic semiconductors attracted the interest of a broad community. This was basically due to the expectations of combining the advantages of semiconductors into spintronics applications, for example. However, the early excitement after the first reports on magnetic order at room temperature appeared, was quickly overwhelmed by doubts on homogeneity issues as well as extra contaminations. On the other hand the broad research done afterwards helped to recognize that, as in graphite, defects, as vacancies (or added nonmagnetic ions) play a crucial role in the observed magnetic order. For recent reviews on DIM in oxides the reader should refer to [43], [53], [54]. Here we restrict ourselves to point out some results regarding DIM due to vacancies, hydrogen and surface states in certain oxides reported recently.

The ground state of cation vacancies (0,V,F centres) in oxides attracted attention already in the 60's and 70's and

there are extensive studies of cation vacancies in simple oxides like Al_2O_3, MgO, SrO, CaO, BeO and ZnO, for a review see, e.g., [55]. A high spin state of the neutral Mg vacancy in MgO was reported in [56], but probably the first observation of a high spin state due to a cation vacancy was reported in a ZnO sample, i.e. due to a Zn vacancy, treated by electron irradiation [57]. In spite of that the possibility to have magnetic order through a minimum amount of vacancies was not recognized at that time.

For undoped ZnO, probably the first hints on the possible role of vacancies in the observed magnetic order were obtained in thin films prepared by pulsed laser deposition (PLD) under partial N_2 atmosphere [58]. This rather preliminary result was confirmed a year later in [59], a study that concluded that neutral Zn vacancies, not O vacancies, produced during the preparation of the film in the PLD chamber should play the main role in the observed magnetic order. Characterization of the lattice defects by x-ray absorption spectroscopy (XANES) at the Zn K-edge in ferromagnetic, pure ZnO films, supported this conclusion [60]. We note that the absolute value of the magnetization of these ferromagnetic thin films ($\sim 10^{-2}$ emu/g) suggests already that the amount of ferromagnetic mass in the films is certainly less than 1%, an indication of the inhomogeneous distribution of defects. Therefore one may still doubt whether bulk characterizations of the films would provide the properties of the magnetic regions. New studies of un-doped ZnO films prepared on silicon and quartz substrates suggested, however, that the ferromagnetism is originated from singly occupied oxygen vacancies, not Zn vacancies, reaching magnetization values of the order of 1 emu/g for ~ 100 nm thick films [61]. The conclusion that oxygen vacancies in ZnO are the reason for the observed magnetic order is at odd with several works cited above. However, in that work [61] no clear analysis of the magnetic impurities in the successive annealing steps was done. Therefore, the subject remains partially controversial.

The possibility of triggering magnetic order due to hydrogen adsorption at the surface of pure ZnO was studied theoretically in [62], [63]. Evidence for surface magnetism in pure ZnO films after hydrogen annealing at $100^\circ - 500^\circ$ was found in [64] together with evidence of the importance of OH-terminated surfaces, supporting theoretical predictions. Interestingly, the FM could be turn on and off after annealing in hydrogen or argon atmosphere. Further support to the possibility of using hydrogen to trigger magnetic order in ZnO came from the change in magnetization [65] as well as in the magnetotransport properties [66] after low energy proton implantation on ZnO single crystals. The obtained magnetization at saturation was ~ 5 emu/g and localized in a near surface region of thickness $\lesssim 20$ nm [65], [66]. The measured anisotropic magnetoresistance (AMR) up to room temperature indicates a spin splitted band as well as a finite spin-orbit coupling [66]. These works indicate that hydrogen should be a good candidate to trigger magnetic order in a more systematic way than with solely vacancies. If the effect is reproducible, triggering magnetic order through hydrogenation of the surfaces of micro- and nanowires of ZnO should be possible.

Not only in ZnO but in several other oxide structures like MgO, $SrTiO_3$, $MgAl_2O_4$, $LaAlO_3$, their surface and upon termination can show magnetic order at room temperature without extra doping. This is the conclusion that was arrived in [67]. In particular the sensitivity of the magnetic signals after acetone or ethanol cleaning of the surface of $SrTiO_3$ substrates indicate a surface origin. The impact of these two liquids on the surface magnetism has been theoretically studied in [68]. Those results indicate that Ti- as well as O-vacancies at the surface play a role in the observed difference between ethanol and acetone influence on the surface magnetism.

The studies in [69] showed that the observed room temperature magnetic order in ZnO:Cu(2%) films can be attributed the magnetic moments arising at the Cu ion, i.e. the d^{10} electronic state of Cu can decrease when coupled to an O-vacancy originating a finite moment coming from the Cu $d-$band; the magnetic moments of O are found opposite oriented to the Cu ones. Actually, a similar explanation was proposed earlier in [70] to explain the ferromagnetism observed in TiO_2:Cu. All these results indicate the important role that vacancies may play after doping non magnetic oxides to trigger magnetic order. Not only vacancies but also dislocations appear to provide a main contribution to the magnetic response of undoped and Mn-doped ZrO_2 films [71].

The role of defects in the magnetic response of oxides goes beyond the nominally nonmagnetic oxides but can be also shown to play a role in magnetic oxides stressing the fact that DIM is a quite general phenomenon. Recent experiments [72] provided evidence for DIM in $ZnFe_2O_4$ samples grown under low O_2 pressure, pointing at the role of oxygen vacancies in the observed magnetism. This is further supported by recently done XMCD measurements and *ab initio* calculations in the framework explained above [73]. All this work demonstrates that a missing oxygen atom between two adjacent Fe^{3+} atoms on B sites leads to a parallel alignment of the Fe moments and therefore a large magnetic moment per unit cell.

We would like to end this section referring to photoconductivity studies, a property that was hardly used in the past to characterize the effects of DIM. The idea is to study the effects of a magnetic field on the photoresistance, a property that depends on the lifetime of photogenerated electrons and this on the particularities of the energy centers inside the gap that are originated by defects. If these defects play a role in DIM, then a magnetic field can influence the photoconductivity. Measurements in magnetic ZnO films [74] revealed that a magnetic field enhances the recombination time of photoexcited carriers, increasing the photoconductivity. In principle this property may be used in the future as a magnetic defect spectroscopy, studying the effect of a magnetic field on the photoconductivity in a broad energy range.

V. Evidence for DIM in other compounds

We note here two different non-oxide materials that after irradiation show a ferromagnetic response. Proton irradiation of MoS_2 revealed magnetic ordering at room temperature when exposed to a 2 MeV proton beam (similar energy than in [32]). The temperature dependence of magnetization displays

ferrimagnetic behavior with an remarkably high Curie temperature of 895 K [75]. The authors suggest that not necessarily a single kind of defect but the combination of magnetic moments arising from different defects, like vacancies, interstitials, deformation and partial destruction of the lattice structure may be necessary to understand the triggered magnetic order. DIM was also observed after neutron irradiation of SiC single crystals [76]. The authors in that work demonstrated that mainly the produced divacancies ($V_{Si}V_C$) appear to be responsible for the observed magnetism. Theoretical studies revealed that extended tails of the defect wave functions induce the long-range coupling between the localized moments caused by the divacancies [76], a further example of the richness of the DIM phenomenon in solids.

VI. Perspectives and Conclusion

Maximum magnetization can be achieved for a certain vacancy concentration, beyond it, the magnetization will reduce and eventually vanishes. This limit provides maximum magnetization values that would hardly surpass that of usual strong ferromagnets. Therefore, the production of large-mass homogeneous magnetic samples with DIM will remain difficult and future activities should concentrate on inducing this phenomenon in rather small samples. Although vacancies will remain an important defect to take care, several studies discussed here (see also [43]) already indicate that doping with non-magnetic elements as H, C, N, etc., appears nowadays an interesting route to achieve high magnetization values and homogeneous samples. Due to the relatively small values of magnetization one tends to believe that DIM is a weak phenomenon, however they are small because of the unidentified mass of the FM regions. Taking into account that $\sim 5\%$ vacancies can trigger magnetic order with $T_C > 300$ K, a comparison with $T_C \simeq 150$ K triggered by $\sim 5\%$ Fe-magnetic ions in Pd [77] indicates that DIM is not a weak but an extraordinarily strong phenomenon.

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