Mn-Stabilized Zirconia: From Imitation Diamonds to a New Potential High-T_C Ferromagnetic Spintronics Material

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From the basis of *ab initio* electronic structure calculations which include the effects of thermally excited magnetic fluctuations, we predict Mn-stabilized cubic zirconia to be ferromagnetic above 500 K. We find this material, which is well known both as an imitation diamond and as a catalyst, to be half-metallic with the majority and minority spin Mn impurity states lying in zirconia's wide gap. The Mn concentration can exceed 40%. The high-T_C ferromagnetism is robust to oxygen vacancy defects and to how the Mn impurities are distributed on the Zr fcc sublattice. We propose this ceramic as a promising future spintronics material.

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Spintronics devices must possess the ability both to generate and to manipulate electronic spin at room temperature and above. To this end a rich expertise has been built up on how to integrate ferromagnetism into semiconductor materials [1]. The best-characterized dilute magnetic semiconductors (DMS), Ga(Mn)As, have Curie temperatures T_C up to 173 K [2]. T_C strongly depends on the sample preparation and Mn concentration, which is low, usually varying between 3 and 7 at. %. A variety of factors continue to keep T_C in these III–V's and other DMS far below room temperature. In the wake of theoretical predictions [3] that ZnO should become ferromagnetic when doped with a transition metal and the experimental discovery of room-temperature ferromagnetism in thin films of cobalt-doped titania, TiO_2 [4], hafnium dioxide, HfO_2 [5,6], and Cr-doped In_2O_3 [7], there is considerable interest in magnetic oxides. The picture here is also complicated. For example, in the wurtzite ZnO, although the solubility of Mn is relatively high [8], $Zn_{1-x}Mn_xO$ is not ferromagnetic unless additional hole doping is provided [3]. In diluted magnetic oxides TiO_2 and HfO_2 the magnetic properties are heavily dependent on the structure and defects [9,10].

As well as a high T_C, a useful attribute for a good spintronics material is a large difference between the majority and minority spin density of states at the Fermi energy so that it can act as the source of spin injection in devices. The material must also be easy to fabricate, stable, and compatible with conventional semiconductors and metals. In this Letter, from the basis of state-of-the-art *ab initio* electronic structure calculations, in which the effects of thermally induced magnetic fluctuations are included, we propose that Mn-doped cubic zirconia, well known both as a catalyst and also as synthetic diamond but as yet untested magnetically, matches all these criteria and is a promising spintronics material. Ceramics such as these also provide an ideal opportunity for the study of ferromagnetism up to high temperatures associated with carrier mediated half-metallicity where there is compatibility with both group IV semiconductors and metals.

Pure ZrO_2 is one of few high dielectric constant and wide-gap insulators and is known to be thermally stable on SiGe [11]. It is being investigated as an insulating gate in complementary metal-oxide semiconductor field effect transistors. The cubic phase is stabilized at room temperature by the addition of 3 to 40 mol. % MnO to ZrO_2 [12]. Our calculations show that manganese-stabilized cubic zirconia (Mn-SZ) remains ferromagnetic to reasonably high temperatures. Epitaxial growth of zirconia thin films on Si, SiGe, Ge [13,14], and, in cubic form, Pt substrates [15] is now easily achievable. From the characterization of ZrO_2 on Si, SiGe, and Ge it seems that ZrO_2 meets all requirements for incorporation into a field effect transistor device. We propose therefore that the feasibility of replacing pure ZrO_2 by Mn-ZrO_2 be investigated for potential spintronics applications.

Our proposition is based on extensive spin-density functional theory (SDFT) calculations, where the local density approximation (LDA) is used for the exchange and correlation effects. We demonstrate for the first time that (i) $Zr_{1-x}Mn_xO_2$ is ferromagnetic up to high temperatures (> 500 K for $x = 25\%$), (ii) this ferromagnetism is robust to oxygen vacancy defects and compositional short-range order, (iii) zirconias doped with other transition metals such as Fe and Co are also high temperature ferromagnets, and (iv) half-metallic properties of zirconia doped with the $3d$ impurities appear. Finally, we find the key electronic and structural factors for optimal doping.

Thanks to their commercial applications much is known about cubic zirconias (e.g., Ref. [16]). The cubic (c) phase

of ZrO_2, which exists between 2370 °C and the melting point, has the fluorite structure with each metal ion in regular eightfold coordinated sites. When doped with other binary oxides, such as Y_2O_3 or MnO, this cubic c phase of zirconia can be stabilized below 1000 K down to room temperature. Cubic zirconias are also well known as synthetic substitutes for diamond. To date, however, all studies of Mn-SZ have focused on its catalytic properties [17] and a study of its magnetism has been neglected.

The fundamental nature of magnetic semiconductors is far from being well understood. Neither widely used phenomenological models [3,18,19] nor advanced *ab initio* descriptions are entirely successful in describing all experimental findings. The energy position of the 3d states of a magnetic impurity is a key issue for finite-temperature magnetism of DMS. In principle, *ab initio* SDFT calculations should result in a parameter-free picture, and the widely used LDA has been proven reliable in predicting ground-state properties of metallic systems and semiconductors. There are numerous successful applications of the LDA to calculations of T_C in DMS (for a recent review, see [20] and references therein). Unlike phenomenological model treatments however, the LDA tends to underestimate the localized character of the magnetic impurity states. Much work has been concerned with the on-site Coulomb correlations. For example, LDA + U [21] and the self-interaction-corrected local spin-density approaches [22] form a bridge between the LDA and the phenomenological picture of DMS [23,24]. Here we describe an extensive study of Mn-stabilized zirconia using the well-established LDA and check our conclusions with preliminary LDA + U calculations. We model the magnetic fluctuations at finite T in terms of "local moments" [25,26]. Two different approaches are used to estimate T_C. (1) Mapping of total energies connected to rigid rotations of the local moments onto the classical Heisenberg model [using both the coherent-potential approximation (CPA) [27] and frozen-magnon approaches [25]] studied in the mean-field approximation gives $k_B T_C = (2/3)\sum_{i\neq j} J_{ij}$, where J_{ij} are exchange integrals between sites (i, j). (2) Evaluation of the lattice Fourier transform of the direct spin correlation function $S(\mathbf{0}) = S(\mathbf{q} = \mathbf{0})$ in the framework of the disordered local moment method (DLM) [26], which avoids the intermediate step of fitting to an effective Heisenberg model, produces $k_B T_C = S(\mathbf{0})/3$.

We use the multiple scattering [Korringa-Kohn-Rostoker (KKR)] theory with the CPA [27] to describe the motion of the electrons through the system. The CPA handles both the local moment disorder as well as the location of the randomly distributed magnetic impurities. Alternatively, the effect of short-range order of impurities is studied using a 12 atom fluorite supercell (corresponding to $Zr_{0.75}Mn_{0.25}O_2$ alloy) using both KKR and augmented spherical wave [28] techniques. Figure 1 shows our estimates of T_C of $Zr_{1-x}Mn_xO_2$ for the range of concentrations

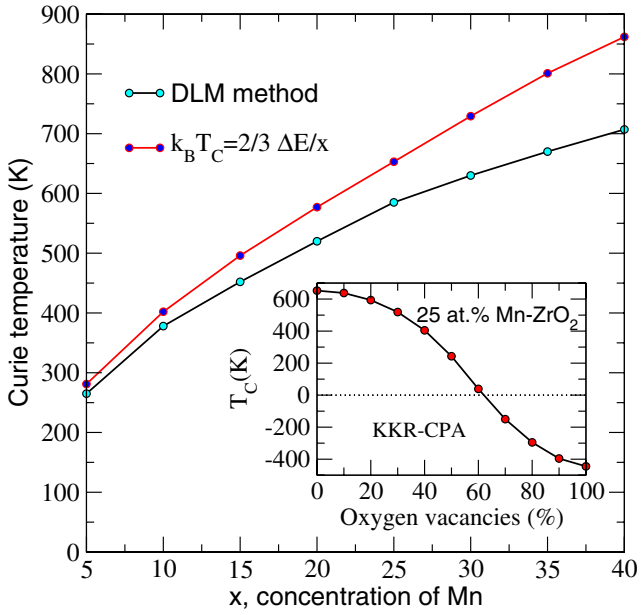

FIG. 1 (color online). The dependence of T_C upon Mn concentration in cubic zirconia using KKR-CPA techniques and DLM theory. T_C extracted from the difference ΔE between total energies of the DLM and ferromagnetic states is also shown. Inset: The variation of T_C of $Zr_{0.75}Mn_{0.25}O_{2-y}\square_y$ as a function of the number of unrelaxed oxygen vacancies, $4y$ (percentage per Mn impurity) where $0 < y < 0.25$.

x at experimental lattice constants using the KKR-CPA technique and the DLM theory [26]. T_C rapidly increases to well above room temperature as x is lifted above 5%. At 25% T_C is 570 K. Although further extensive work is in progress to explore the effects of electron correlation effects beyond the LDA which might be important in these oxides, our preliminary results using the LDA + U method [21] combined with the CPA for the $x = 25\%$ Mn-SZ are that these effects raise T_C by about 15%.

A similar high T_C of 540 K is found from our frozen-magnon LDA supercell calculations for ordered Zr_3MnO_8 [29]. This suggests that the magnetic properties of Mn-stabilized cubic zirconia are rather robust and insensitive to how the Mn atoms are distributed over the fcc Zr sublattice. We show the electronic structure of cubic zirconia doped with several different transition metal impurities, i.e., $Zr_{0.75}M_{0.25}O_2$ with $M =$ Cr, Mn, Fe, and Co, and by artificially altering the Fermi energy, we explore how the further addition of nonmagnetic donors or acceptors affects T_C. The results are shown in Fig. 2; the nominal (correct) number of electrons in the system corresponds to $n = 0$. Negative values of T_C reflect antiferromagnetic rather than ferromagnetic ordering at low temperatures. For $x =$ 25 at. % and $n = 0$, the highest T_C of 540 K is obtained for both the Mn-SZ and Co-SZ systems followed by Fe-SZ (400 K), while the negative T_C of Cr-SZ reveals its antiferromagnetic tendency. For Mn-SZ, T_C at $n = 0$ is near the peak position, and hence any additional codoping is

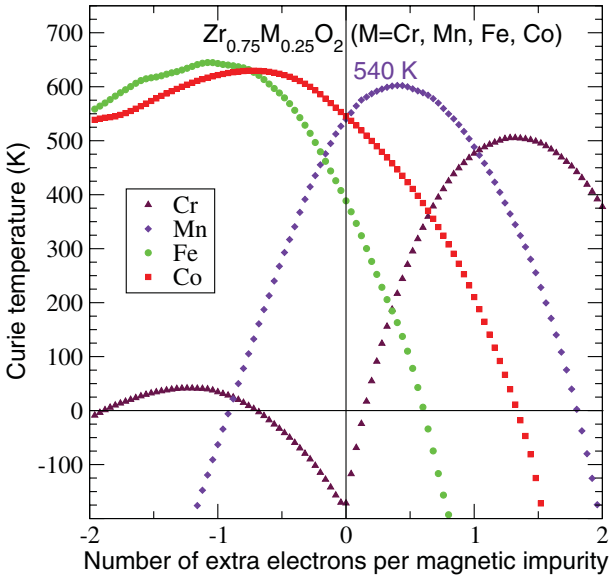

FIG. 2 (color). The Curie temperatures of $Zr_{0.75}M_{0.25}O_2$ (M = Cr, Mn, Fe, Co) ceramics from frozen-magnon calculations. n = 0 corresponds to the nominal (correct) electron number. The variation of n corresponds to modeling extra doping. Negative values of T_C reveal antiferromagnetic ordering tendencies.

unlikely to enhance T_C. For the Fe-SZ and Co-SZ systems, however, codoping with extra hole carriers should drive T_C above 600 K.

The spin-resolved density of states (DOS) of Mn-SZ (Fig. 3) in its ferromagnetic state shows a pronounced half-metallicity. Its origin comes from the Hund rule that the majority spin 3d impurity states are fully occupied. The local magnetic moment on the site Mn is 3.45μ_B and is weakly dependent upon concentration x. The minority spin states lie partially in zirconia's fundamental band gap. For the sequence of dopants Cr, Mn, Fe, and Co these states are increasingly occupied as they shift closer to the host valence band. For each spin, there are two impurity DOS peaks above the top of the valence band separated by the pseudogap, which can be associated with the e_g-t_{2g} splitting expected from a simple ligand field model of the bonding in cubic ZrO_2. Inspecting the DOS of Mn-SZ and Fe-SZ shows both these systems to be half-metallic at zero temperature. In Co-SZ the e_g-like minority spin states of Co are partially occupied making the system metallic. Cr-SZ is an insulator since its completely filled minority spin e_g subband is separated from the empty t_{2g} one.

Figure 4 shows the dependence of the calculated Mn-SZ's T_C on volume and Mn concentration x. The lattice parameter of zirconia decreases from 5.11 to 5.044 Å at 30 at. % Mn [12]. The theoretical values (also in Fig. 4) are in reasonable agreement with the experiment.

The final part of our investigation concerns the sensitivity of the magnetism in Mn-SZ to the presence of oxygen vacancies [17], which are natural defects in doped ceramics. The electronic structure of Mn and the range of valences attributed to it in different materials makes a simple ionic charge analysis of Mn-SZ and a consequent estimate of the number of vacancies difficult. Instead we compare Mn-SZ with a related well studied system, yttria-stabilized cubic zirconia, Y-SZ, where the oxidation state of yttrium is more easily defined. Y-SZ's well-known high ionic conductivity is connected with its large number of oxygen vacancies (one for every pair of Y atoms). No such high ionic conductivity is known for Mn-SZ, so we make the reasonable assumption that it has a smaller vacancy-to-dopant ratio. The inset of Fig. 1 shows our KKR-CPA calculations of T_C for 25% Mn-ZrO_2 as a function of the O vacancy concentration from the difference in total en-

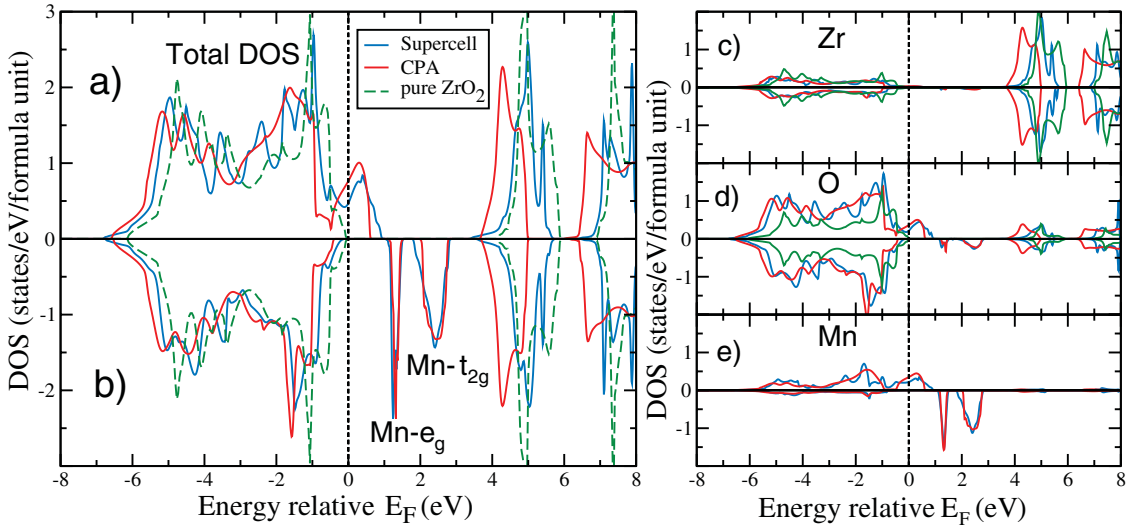

FIG. 3 (color). (a),(b) Spin-resolved DOS of $Zr_{0.75}Mn_{0.25}O_2$ [supercell (blue solid line) and CPA (red solid line) and pure ZrO_2 (green dashed line)]. (c)–(e) Spin- and sites-resolved DOS for Zr, O, and Mn, respectively.

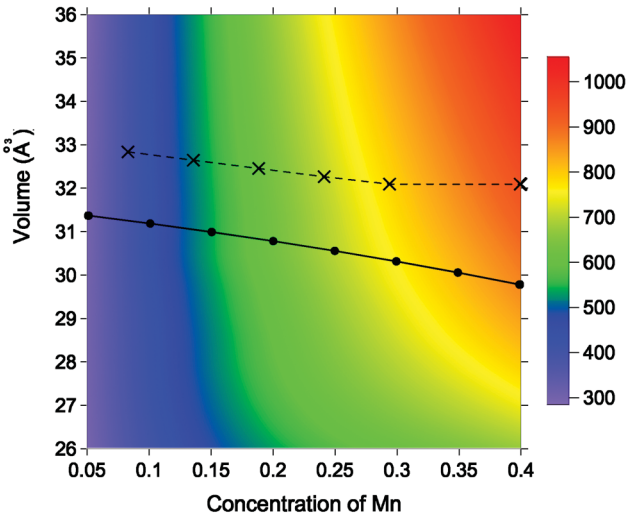

FIG. 4 (color). T_C of $Zr_{1-x}Mn_xO_2$, calculated with the KKR-CPA, is plotted as a contour map versus x and volume. The theoretical equilibrium volumes (solid line) for each x are plotted together with the experimental data (dashed line).

ergies of the DLM and ferromagnetic states. T_C remains high when there is up to one oxygen vacancy for every three Mn ($4y < 33\%$). Beyond that, T_C decreases near linearly so that when the number of vacancies approaches the number of Mn impurities ($4y > 65\%$) the system is no longer ferromagnetic. For $4y = 50\%$, the system, comparable to that of Y-SZ, should still be ferromagnetic and a half-metal. Of course it is possible that the presence of vacancies leads to large displacements of atoms from their ideal lattice positions. To investigate this we have carried out further calculations where one oxygen is removed from a Zr_3MnO_8 supercell. The atoms surrounding the vacancy are then shifted towards the vacancy by 7%. We find only a marginal change in the magnetic properties for this structure.

From the *ab initio* basis of our work we surmise that manganese-stabilized cubic zirconia can become a room-temperature single-spin injector. Our results are obtained using three different theoretical approaches that are based on different physical models. In particular, the assumed patterns of the impurity distributions differ radically. The insulating wide gap of the host ZrO_2 plays no important role when the magnetic dopant level is high since the electronic density of states is completely spin polarized at the Fermi level. The conductivity, therefore, will be dominated by this metallic single-spin channel. Surprisingly, the magnetic properties of Mn-stabilized zirconia, a material widely used in catalysis, have not been studied up to now. We suggest that such studies may have real technological as well as fundamental relevance. Mn-SZ could perhaps be incorporated into a spin field effect transistor. Moreover, we infer that the high levels of Mn in Mn-stabilized zirconia will prevent it from following the fate of other spintronics materials which have not been found to be magnetic at room temperature.

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