Model for vacancy-induced ferromagnetism in oxide compounds.

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We propose a model with few parameters for vacancy-induced ferromagnetism based on a correlated model for oxygen orbitals with random potentials representing cation vacancies. For certain potentials, moments appear on oxygen sites near defects. Treating the randomness exactly, we calculate the magnetic couplings between moments, the Curie temperature and spin and charge densities as a function of the potential, the density of vacancies, and correlation strength. For physically reasonable parameters this predicts Curie temperatures well above room temperature for small concentrations of vacancies. We discuss our results in relation to questions of stability and reproducibility raised in experiments. To circumvent the difficulties of controlling intrinsic defects, we propose specific non-magnetic host doping that could be, for example, substituted for cations in HfO\textsubscript{2} or ZrO\textsubscript{2}.

A number of exciting, but puzzling, effects when ferromagnetism is seen in unexpected places, are apparently unrelated to traditional transition metal magnetism: in oxides such as HfO\textsubscript{2}, ZrO\textsubscript{2}, CaO, ZnO, and related materials such as hexaborides \textsuperscript{2} (CaB\textsubscript{6}) and even irradiated graphite \textsuperscript{4,5}. Thin films of materials which in bulk have neither magnetic moments nor magnetic order, may be ferromagnetic well above room temperature \textsuperscript{2,6}. HfO\textsubscript{2} or ZrO\textsubscript{2}, are both wide-band insulating material with high dielectric constant; the possibility of making them ferromagnetic could widen their possible application in the field of spintronics. There are analogies to the discovery \textsuperscript{2} that the doping by a small amount of magnetic impurities could lead to relatively high Curie temperature in III-V semiconductors. There are, apparently, however too few magnetic impurities in the ZrO\textsubscript{2} films, for example, to explain the magnetism and the cation (nominally Zr\textsuperscript{4+}) should be in a non-magnetic d\textsuperscript{0} configuration. The term “d\textsuperscript{0}” ferromagnetism was coined to describe this general phenomenon. There are suggestions that the ferromagnetism is related to intrinsic cation or anion vacancies, and that this may be a path to new ferromagnets. \textsuperscript{2,3,5} Band structure calculations \textsuperscript{10,11} supported the idea that vacancies can induce local moments on neighboring atoms. What is lacking, especially as the experimental results are still unstable, is a quantitative theory of long-range ferromagnetic order of any such moments. This can define the important parameters, for example the nature and concentrations of vacancies and their effective doping. The aim of the present letter is to provide a model for vacancy induced ferromagnetism explaining Curie temperatures at room temperatures. This can also help understand instabilities, and propose new materials where controlled substitutions could replace the vacancies. Point defects have been suggested several times as a mechanism for localized moments \textsuperscript{2,3,5,12} and ferromagnetism in oxides. While oxygen vacancies were originally suggested as the source of magnetism in HfO\textsubscript{2}, \textsuperscript{1} density functional calculations including various defects \textsuperscript{10} found no evidence for moments around such defects. A large magnetic moment was, however, found in partially depleted oxygen orbitals around Hf vacancies. Couplings were estimated between two defects confined within a supercell. This is not sufficient to estimate properly the Curie temperature as a function of vacancy concentration which require couplings at all distances. We propose a theory where dependence on concentration and also the effective doping of different defects can be studied. We start from the idea of vacancy-induced moments and construct a model, with only few free parameters, in which we can estimate not only the temperature dependence of local moments, but also the couplings required to maintain long-range ferromagnetic order at the low concentrations relevant to the experiments. We can also calculate the thermodynamics and dynamical spin correlations for future systematic experimental investigations. We formulate the problem for the cases of cation vacancies in oxides such as HfO\textsubscript{2}, ZrO\textsubscript{2} and CaO, but the aim is to explore what may be a more general phenomenon, in which a vacancy or substitutional defect creates an extended magnetic moment on neighboring atoms. While there are similarities to the theory of magnetism in diluted magnetic semiconductors but there the substitutional impurities immediately provide localized magnetic moments which interact via the itinerant carriers of the (doped) host. Here the moment is induced on several non-magnetic oxygen atoms of

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the original host and their is no clear separation between the holes forming the moment and those mediating the interactions.

We describe this via a single correlated band of oxygen orbitals, with random potentials representing the influence of the randomly introduced vacancies on neighboring cation orbitals. The oxygen atoms are on a regular lattice, taken to be cubic for simplicity. In the pure host, the parameters can be those calculated for the filled oxygen-dominated bands. The cations in the pure material are assumed to be at the center of each elementary cube of the lattice. A concentration \( x \) of cation vacancies is modeled by choosing randomly the positions of the 8 neighboring oxygens (O1 and O2)\(^1\). To ease comparison with Local Density Approximation density of states of neighboring oxygens (O1 and O2)\(^1\). To ease comparison with Local Density Approximation density of states we took \( V_i = V \) on four neighbors and \( V_i = \frac{V}{4} \) on the other four. \( V \) is a free parameter. The hole density is taken to be a variable \( n_{\text{hh}} \). In the simplest picture (only cation vacancies) \( n_{\text{hh}} \) is \( 4x \) for HfO\(_2\) and ZrO\(_2\) (cation 4+) and \( 2x \) for CaO or ZnO (cation 2+). In numerics we quote \( U \) and \( V \) in terms of the host bandwidth \( W = 12t \). For ZrO\(_2\) we take \( W = 7 \) eV from the calculated bandwidth of the p band just below the Fermi level and \( U \sim 3 \) eV as estimated for the Hubbard parameter for oxygen p orbitals \( U_{pp} \) in copper oxides \(^{11}\).

We treat the correlated disorder exactly as the unrestricted Hartree-Fock (UHF) approximation is applied in real space for each configuration of disorder, sampled over many configurations. Comparison to exact results indicate that UHF works well for ground state properties in random systems.\(^{12,13}\) All calculations presented were for sufficiently large systems (typically \( \sim 16^3 \) sites) that finite size effects are negligible. In Fig. 1 we show the single particle density of states and the distributions of both hole density and induced local moments for fixed \( U = 0.4 \) W, \( n_{\text{hh}} = 0.12, x = 4\% \) and three values of \( V = 0.2, 0.45, 0.8 \) W. The Fermi energy is at zero. For small \( V \) there are no local magnetic moments. As \( V \) increases, moments appear (\( V \geq 0.28 \) W) as the charge and spin distributions develop structures localised around the vacancies (right column). Later (\( V \approx 0.45 \) W), a well-defined impurity band for the minority band splits from the valence band. The first peak in the distributions (right column), at low densities, corresponds to sites with \( V_i = V/3 \) and the second broad peak to \( V_i = V \). As \( V \) further increases, we also observe a splitting of the density of states in the majority band and holes concentrated around the vacancies, providing saturated localized moments. Note that the total moment on each cube centered on a vacancy is almost saturated (\( \sim 3\mu_B \)) for \( V \geq 0.4 \) W. We now estimate the magnetic couplings at all distances between the different moments, by UHF calculation of the carrier Green functions \( G_{ij}^{\sigma} \). We will subsequently make a self-consistent local random phase approximation (SC-LRPA) on the effective random Heisenberg model, which was successful for diluted magnetic semiconductors. Each spin of the Heisenberg model will represent the total spin around one vacancy. Calculation of the exchanges is made by an extension of the method of Lichtenstein et al.\(^{13}\). They determined the exchange between any pair of (local) moments by calculating the change in energy when fields are applied to the sites of the two moments. Here, the fields are applied to two differing directions, the first to all the \( N_S = 8 \) neighbors \( i \) of one defect \( a \); the second to the neighbors \( j \) of
FIG. 2: (Color online) Magnetic couplings (in Kelvin) as a function of separation of vacancies, in units of the cubic lattice spacing, for different values of the potential $V$. In each case $U = 0.4W$, $x = 0.04$ and $n_h = 0.12$ as in Fig. 1.

Thus we calculate the exchange energies by summing the contribution of $N_S \times N_S$ pairs of terms $J_{a,b} = \sum_{\text{left }, j} J_{i,j}$ where

$$J_{i,j} = -\frac{1}{\pi} \int_0^{E_F} \Sigma_i(\omega)G^\uparrow_{i,j}(\omega)\Sigma_j(\omega)G^\downarrow_{j,i}(\omega)d\omega$$

In UHF the local potential $\Sigma_i = U(n^\uparrow_i - n^\downarrow_i)$.

The dilute Heisenberg model is defined with spins centered on the position of the randomly placed vacancies and interacting by the $J_{a,b}$. $\mathcal{H} = -\sum_{a,b} J_{a,b} S_a \cdot S_b$ with $S_a \sim 3\mu_B$ are large enough to be treated classically, allowing application of the local force theorem. In Fig 2 we show the calculated couplings averaged over different impurity configurations. We vary the potential $V$ and fix $x = 4\%$ and $n_h/x = 3$. This last choice (rather than 4) will be made clearer by the figures following. For small $V$ the couplings oscillate with distance, but with antiferromagnetic nearest neighbor coupling. As $V$ increases the couplings become more ferromagnetic but with further increase some become antiferromagnetic again. Thus from Fig. 2 there is a range of values $V$ where the couplings, while fluctuating, are all ferromagnetic ($J(r) \geq 0$). This is associated in Figure 1(b) with the incipient development of a visible impurity band just at the band edge. This ferromagnetic bias in the “RKKY-like” oscillations corresponds to the resonant form of the impurity band[19].

We now treat the thermodynamics within SC-LRPA[17]. We recall that randomness is treated exactly, essential at the low concentrations relevant here. In Fig. 3 we show the Curie temperatures ($T_C$) calculated from the exchanges as a function of $V$. It is seen that there is a well-defined region where $T_C$ is above room temperature. Comparing to Figs. 1 and 2 we see that for $V$ either too small or too large, $T_C$ vanishes because the couplings are frustrated by RKKY-type oscillations (small $V$) or superexchange (large $V$). As seen in Fig 2, near the optimal value ($V=0.45W$) the couplings are largest and do not change sign. Remark that at that value (see Fig 1(b)) the impurity band is very similar to that of doped Ga(Mn)As[20]. Optimal values of $V$ have high $T_C$ for the same reason, the position of the impurity band, that Ga(Mn)As has a larger $T_C$ than Ga(Mn)N and In(Mn)As which resemble more cases (c) and (a) respectively[17].

In Fig. 4 we fix the density of defects and $V$ near the optimal value of Fig. 3 and vary the number of holes per
vacancy. Below and above critical values of $n_h/x$ there is no ferromagnetism. There is a window of concentrations where $T_C$ becomes very large. The reason for instability outside the window is for low carrier densities, dominant antiferromagnetic superexchanges and for high densities, RKKY-like oscillations. Note that for the points where $T_C = 0$ our calculation predicts that are still local moments, in agreement, for example, with \textit{ab-initio} calculations\cite{9} for defects in CaO, but no long-range ferromagnetic order. Interestingly, the formal charges of vacancies in HfO$_2$ or CaO are near the edges of stability of ferromagnetism for the parameters chosen. This may suggest an explanation for the extreme sensitivity of current results to sample history. Note that a more direct comparison with experiments would require a precise knowledge of the parameters and the concentrations of all defects including especially Oxygen vacancies. Oxygen vacancies, would \textit{decrease} the effective hole density and could stabilize $T_C$ for HfO$_2$. The figure also suggests that a promising avenue for stabilizing or increasing the Curie temperature experimentally may be to use non-magnetic substitution of Hf(Zr) by Li, Na, K, Rb or Cs … rather than Hf(Zr) vacancies which are difficult to control.

Our results are based on a Hartree-Fock approximation that tends to overestimate the tendency to ferromagnetism in some homogeneous itinerant models. Nonetheless Kanamori\cite{21}, Tasaki\cite{22} and others have shown that in “flat band” models in which there is a peak in the density of states with a relatively flat background, ferromagnetism is indeed possible. Because of the vacancies, our model resembles a flat band model. We remark that degeneracy of orbitals\cite{8} is not required, as the moments are stabilized by the molecular fields of other moments. Note that screening effects which reduce the effective $U$ by the $t$ matrix\cite{21} are important when $U \gg W$ which is the not the case here. In addition, we have verified that the results vary little with $t'/t$ and $U$ in broad ranges, $0.2 \leq U/W \leq 0.6$ and $0.1 \leq t'/t \leq 0.6$. In contrast $T_C$ is very sensitive to both $V$ and $n_h/x$ which are the most relevant parameters. We have also seen that below typically 1% no ferromagnetism is possible.

In ref.\cite{12} the equilibrium density of cationic vacancies was estimated as 0.03%. Thus higher non equilibrium concentrations are very likely needed, as are quite possible in films. However a more promising avenue for “d$^0$” ferromagnetism would be the substitutional approach.

To conclude, we present a model which catches the essential ingredients for vacancy- or substitutional-induced ferromagnetism of the oxygen holes. Our calculations shows that Curie temperatures above room temperature are feasible for a few per cent of vacancies or substitutions. The sensitivity of “d$^0$” samples may be explained by the proximity of the doping to the stability boundary. The underlying mechanism is close to that of diluted III-V semiconductors: enhanced ferromagnetic couplings between resonant impurity levels at parameters just at the point where the impurity states split off from the valence band. It would be interesting to measure the profile of the density of states (e.g. by photoemission) to see whether it does indeed correspond to the proposed picture (see Fig. [center row]). As Curie temperatures are non-monotonic in both the strength of the potential and the doping, accurate characterization may be needed in order to find useful ferromagnetic materials. \textit{Ab-initio} results for the effective Hamiltonian could help refine the choice of compound. Our calculation, Figure\cite{10} suggests that for HfO$_2$ (ZrO$_2$), site substitution of the Hf(Zr) by elements differing by 3 in formal charge, i.e. Group 1A of the periodic table would be a promising direction. This may be attractive since it can be realized in bulk as well as films.

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