Model for Vacancy-Induced d^0 Ferromagnetism in Oxide Compounds

Georges Bouzerar[1,*] and Timothy Ziman[2,†]
[1]*Laboratoire Louis Néel, CNRS, 25 avenue des Martyrs, Boîte Postale 166 38042 Grenoble Cedex 09, France*
[2]*Institut Laue Langevin and CNRS, Boîte Postale 156 38042 Grenoble, France*

(Received 1 March 2006; published 26 May 2006)

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 nonmagnetic host doping that could be, for example, substituted for cations in HfO_2 or ZrO_2.

DOI: 10.1103/PhysRevLett.96.207602 PACS numbers: 77.80.Bh, 71.10.−w, 75.30.Et

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_2, ZrO_2 [1], CaO, ZnO, and related materials such as hexaborides [2] (CaB_6) and even irradiated graphite [3,4]. Thin films of materials, which in bulk have neither magnetic moments nor magnetic order, may be ferromagnetic well above room temperature [5,6]. HfO_2 or ZrO_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 [7] that the doping by a small amount of magnetic impurities could lead to relatively high Curie temperature in III-V semiconductors. Apparently there are, however, too few magnetic impurities in the ZrO_2 films, for example, to explain why the magnetism and the cation (nominally Zr^{4+}) should be in a nonmagnetic d^0 configuration. The term "d^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 [8,9]. Band structure calculations [10–12] 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 this Letter is to provide a model for ferromagnetism induced by a vacancy mechanism 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 [8,9] and ferromagnetism in oxides. While oxygen vacancies were originally suggested as the source of magnetism in HfO_2 [6], density functional calculations including various defects [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 Hamiltonian, with a limited number of free parameters, in which we can estimate not only the temperature dependence of local moments, but also the magnetic couplings required to maintain long-range ferromagnetic order at the low concentrations relevant to the experiments. We can use this model to 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_2, ZrO_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, there the substitutional impurities immediately provide localized magnetic moments which interact via the itinerant carriers of the (doped) host. Here [9] the moment is induced on several nonmagnetic oxygen atoms of 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 additional random potentials representing the influence of the randomly introduced vacancies on neighboring cation orbitals. The oxygen atoms are on a regular

© 2006 The American Physical Society

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 cube centers. Thus a "defect" does not alter the regular geometry of the oxygen lattice but introduces attractive potentials on the 8 neighboring oxygen orbitals of the cube center chosen. The usual Hubbard Hamiltonian on a regular lattice has an extra term which is a random, but *locally correlated*, potential:

$$\mathcal{H}_0 = -\sum_{i,i',\sigma} t_{i,i'}(\mathbf{c}_i^{\dagger\sigma}\cdot\mathbf{c}_{i'}^{\sigma} + \mathbf{c}_i^{\sigma}\cdot\mathbf{c}_{i'}^{\dagger\sigma}) + \sum_i U\mathbf{n}_i^{\uparrow}\mathbf{n}_i^{\downarrow} - V_i(\mathbf{n}_i^{\uparrow} + \mathbf{n}_i^{\downarrow})$$

where $c^\dagger$ (c) operators create (destroy) electrons in the oxygen orbitals. V_i are attractive on sites adjacent to the vacancies, corresponding to attraction of the holes. Nearest neighbor hopping $t_{i,j} = t$ everywhere except between pairs of sites neighboring the same vacancy for which $t_{i,j} = t'$. Defects in Hf or ZrO_2 have two inequivalent sets of neighboring oxygens (O1 and O2) [10]. To ease comparison with local-density approximation local density of states we took $V_i = V$ on four neighbors and $V_i = \frac{V}{3}$ on the other four. V is a free parameter. The hole density is taken to be a variable n_h. In the simplest picture (*only* cation vacancies) n_h 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 in Ref. [13] and $U \sim 3$ eV as estimated for the Hubbard parameter for oxygen p orbitals U_{pp} in copper oxides [14].

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 approximations work well for ground state properties in random systems [15,16]. 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, $n_h = 0.12$, $x = 4\%$, 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 localized 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 exchange interactions at all distances between the different moments, by UHF calculation of the carrier Green functions $G_{ii'}^{\sigma}$. We will subsequently make a self-consistent local random phase approximation (SC LRPA) on the effective random Heisenberg model [17], 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.* [18]. They determined the

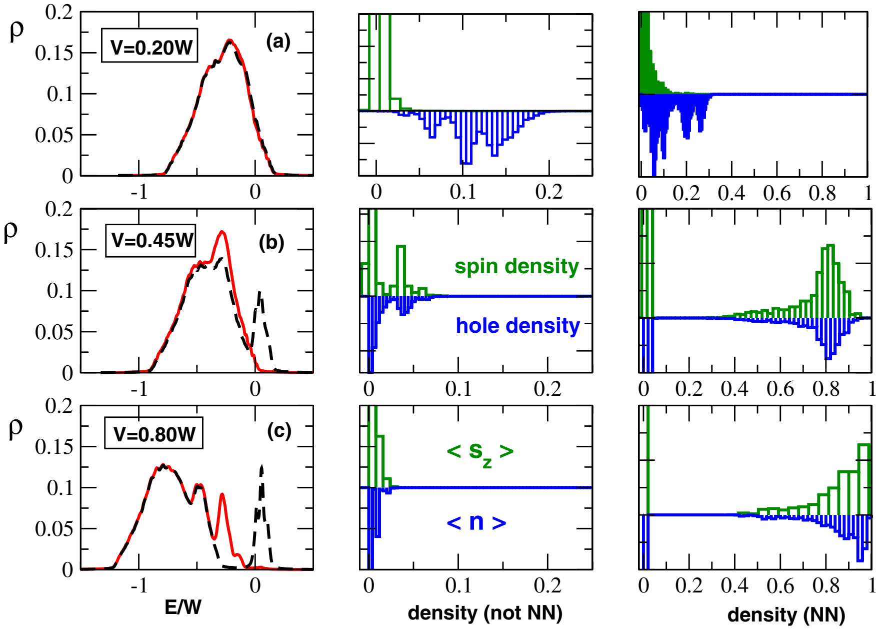

FIG. 1 (color online). Density of states (left), and distributions of charge and magnetic moments (middle and right columns). The right column shows the densities projected onto oxygen neighboring vacancies (NN); the middle column other oxygens (not NN). The majority and minority bands (left column) are continuous and dashed, respectively. Energies are in units of bandwidth measured from the Fermi level, the moments in units of μ_B.

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 the second b. Thus we calculate the exchange energies by summing the contribution of $N_S \times N_S$ pairs of terms $\mathcal{J}_{a,b} = \sum_{i\epsilon a, j\epsilon b} \mathcal{J}_{i,j}$ where

$$\mathcal{J}_{i,j} = -\frac{1}{\pi}\Im\int_{\infty}^{E_F}\Sigma_i(\omega)G^{\uparrow}_{i,j}(\omega)\Sigma_j(\omega)G^{\downarrow}_{j,i}(\omega)d\omega.$$

In UHF the local potential $\Sigma_i = U(n_i^{\uparrow} - n_i^{\downarrow})$.

The dilute Heisenberg model is defined with spins centered on the position of the randomly placed vacancies and interacting by the $\mathcal{J}_{a,b}$. $\mathcal{H} = -\sum_{a,b}\mathcal{J}_{a,b}S_a \cdot S_b$ with S_a the total spin around each vacancy. $S_a \sim 3\mu_B$ 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 Fig. 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 ($V = 0.45$ W) 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 Curie temperatures 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 [Figs. 1(c) and 1(a)], respectively [17].

In Fig. 4 we fix the concentration 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 concentration 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 indicating that $T_C = 0$ our calculation predicts that there are still local moments, in agreement, for example, with *ab initio* calculations [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 *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 nonmagnetic 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

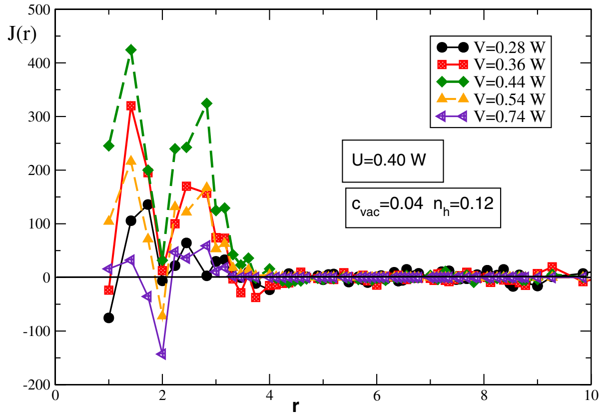

FIG. 2 (color online). Magnetic couplings (in Kelvin) as a function of separation of vacancies, in units of the cubic lattice spacing, for different values of the potential V. In each case $U = 0.4$ W, $x = 0.04$, and $n_h = 0.12$ as in Fig. 1.

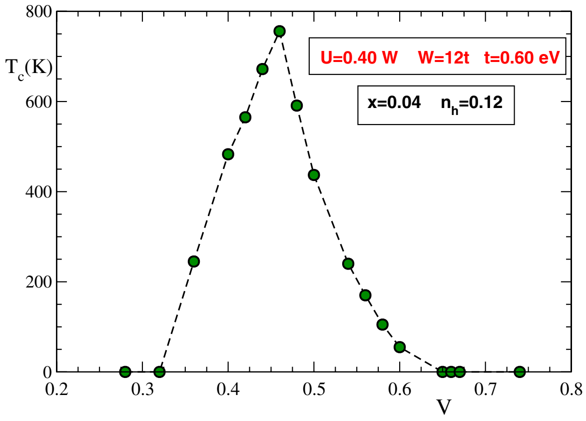

FIG. 3 (color online). Curie temperature as a function of the potential V (in units of W). Other parameters as in Fig. 2.

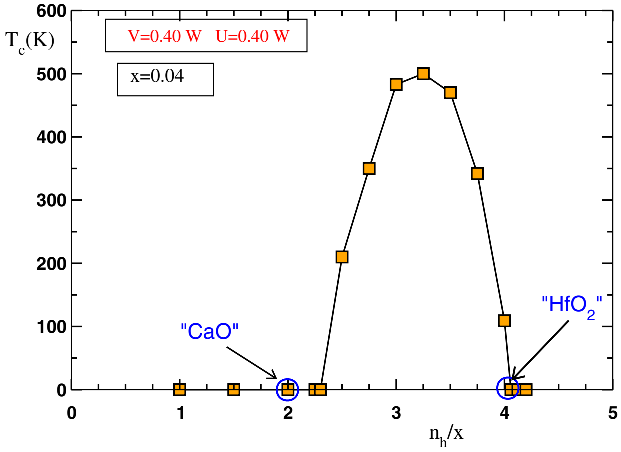

FIG. 4 (color online). Curie temperature for different carrier densities for 4% defects. $V = 0.4$ W, $U = 0.4$ W are fixed.

in some homogeneous itinerant models. Nonetheless Kanamori [21], Tasaki [22] and others [23–25] 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 local orbitals [9] 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 [21], are important when $U \gg W$ which is 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. [12] the equilibrium density of cationic vacancies was estimated as 0.03%. Thus higher nonequlilibrium 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 show that Curie temperatures above room temperature are feasible for a few percent of vacancies or substitutions. The extreme sensitivity of d^0 materials to sample quality 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. 1 center row). As Curie temperatures are nonmonotonic in both the strength of the potential and the doping, accurate characterization may be needed in order to find useful ferromagnetic materials. *Ab initio* results for the effective Hamiltonian could help refine the choice of compound. Our calculation, Fig. 4, 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.

---

*Email address: georges.bouzerar@grenoble.cnrs.fr
†Email address: ziman@ill.fr

[1] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).
[2] D. P. Young *et al.*, Nature (London) **397**, 412 (1999).
[3] T. L. Makarova *et al.*, Nature (London) **413**, 716 (2001).
[4] P. Esquinazi *et al.*, Phys. Rev. B **66**, 024429 (2002).
[5] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **93**, 177206 (2004).
[6] J. M. D. Coey, M. Venkatesan, P. Stamenov, C. B. Fitzgerald, and L. S. Dorneles, Phys. Rev. B **72**, 024450 (2005).
[7] H. Ohno, Science **281**, 951 (1998).
[8] A. M. Stoneham, A. P. Pathak, and R. H. Bartram, J. Phys. C **9**, 73 (1976).
[9] I. S. Elfimov, S. Yunoki, and G. A. Sawatzky, Phys. Rev. Lett. **89**, 216403 (2002).
[10] C. Das Pemmaraju and S. Sanvito, Phys. Rev. Lett. **94**, 217205 (2005).
[11] R. Monnier and B. Delley, Phys. Rev. Lett. **87**, 157204 (2001).
[12] J. Osorio-Guillen, S. Lany, S. V. Barabash, and A. Zunger, Phys. Rev. Lett. **96**, 107203 (2006) (We thank a referee for this recent reference).
[13] X. Zhao and D. Vanderbilt, cond-mat/0301016.
[14] A. K. McMahan, J. F. Annett, and R. M. Martin, Phys. Rev. B **42**, 6268 (1990).
[15] G. Bouzerar and D. Poilblanc, Phys. Rev. B **52**, 10 772 (1995).
[16] B. Reusch and H. Grabert, Phys. Rev. B **68**, 045309 (2003).
[17] G. Bouzerar, T. Ziman, and J. Kudrnovský, Europhys. Lett. **69**, 812 (2005); Appl. Phys. Lett. **85**, 4941 (2004); Phys. Rev. B **72**, 125207 (2005).
[18] A. I. Lichtenstein, M. I. Katsnelson, and V. A. Gubanov, J. Phys. F **14**, L125 (1984); M. I. Katsnelson and A. I. Lichtenstein, Phys. Rev. B **61**, 8906 (2000).
[19] R. Bouzerar, G. Bouzerar, and T. Ziman, Phys. Rev. B **73**, 024411 (2006).
[20] J. Kudrnovský, I. Turek, V. Drchal, F. Maca, P. Weinberger, and P. Bruno, Phys. Rev. B **69**, 115208 (2004).
[21] J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).
[22] H. Tasaki, Phys. Rev. Lett. **75**, 4678 (1995).
[23] Y. Nagaoka, Phys. Rev. **147**, 392 (1966).
[24] A. Mielke, Phys. Rev. Lett. **82**, 4312 (1999).
[25] F. J. Ohkawa, Phys. Rev. B **65**, 174424 (2002).