

Possible Path to a New Class of Ferromagnetic and Half-Metallic Ferromagnetic Materials

I. S. Elfimov,¹ S. Yunoki,¹ and G. A. Sawatzky^{1,2}

¹*Solid State Physics Laboratory, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

²*Department of Physics and Astronomy, University of British Columbia, 6224 Agricultural Road, Vancouver, British Columbia, Canada V6T 1Z1*

(Received 24 May 2002; published 4 November 2002)

We introduce a path to a possibly new class of magnetic materials whose properties are determined entirely by the presence of a low concentration of specific point defects. Using model Hamiltonian and *ab initio* band structure methods we demonstrate that even large band gap nonmagnetic materials as simple as CaO with a small concentration of Ca vacancies can exhibit extraordinary properties. We show that such defects will initially bind the introduced charge carriers at neighboring sites and depending on the internal symmetry of the clusters so formed, will exhibit “local” magnetic moments which for concentrations as low as 3% transform this nonmagnetic insulator into a half-metallic ferromagnet.

DOI: 10.1103/PhysRevLett.89.216403

PACS numbers: 71.55.-i, 75.10.-b, 75.75.+a

The recent discovery of ferromagnetism with high transition temperatures and very small magnetic moments in the hexaborides [1], Co substituted TiO₂ [2], and Co substituted ZnO [3] has opened a lively discussion regarding the role of defects in transforming insulating nonmagnetic compounds into ferromagnets with interesting properties. In the hexaborides Monnier and Delley demonstrated, using density functional band structure approaches, that neutral B₆ vacancies in a superlattice can result in a ferromagnetic ground state even for a low density of such defects [4]. We note that the nominal valence of the B₆ clusters in fairly ionic materials such as CaB₆ is 2− and so two electrons are needed to charge compensate for such a B₆ vacancy. It is also interesting to note that substituting divalent Co for a tetravalent Ti in TiO₂ also can be compensated with two holes in the oxygen 2*p* valence bands which could be bound impurity states in close proximity to the Co impurity. These observations may remind some that in hydrocarbon molecules with ring structures Longuet-Higgins predicted magnetic ground states due to a kind of molecular Hund's rule coupling well known in atoms [5]. This property has in fact been used in the past by Torrance *et al.* [6] in attempts to make organic molecular ferromagnets. More recently Eskes has used a Hubbard model calculation of ring systems and clusters to demonstrate again a kind of molecular Hund's rule coupling for orbitally degenerate states, leading to very stable magnetic (spin triplet) ground states for either two electrons or two holes, in particular, geometries [7].

In the present Letter we report on the influence of dilute divalent cation vacancies in oxides with the rock salt structure. We predict that such systems have ferromagnetic ground states with small magnetic moments but possibly high transition temperatures. For 3.125% Ca vacancies in CaO local density approximation (LDA) band structure calculations predict a half-metallic ferromagnetic ground state which if correct could play an

important role in the modern field of spintronics and opens a path to a whole new class of ferromagnetic materials. Before presenting the band structure calculations we discuss the physics we believe to be responsible for the magnetic behavior found. In the rock salt structure the cations are surrounded by an octahedron of anions with filled valence *p* bands as shown in Fig. 1. As also shown, the σ -bonding anion *p* orbitals with lobes directed to the cation site would be the most energetically favorable orbitals to accommodate the holes needed to charge compensate a cation vacancy at the center of such an octahedron. Because of the negative effective charge

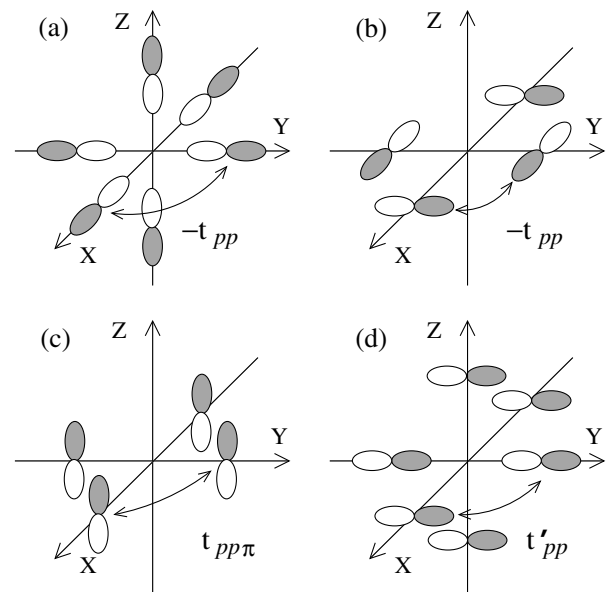


FIG. 1. An artist's concept of the oxygen σ - (a) and π -bonding (b),(c) orbitals relative to the O-vacancy bond direction surrounding a Ca vacancy. Also shown are the definitions of the hopping integrals (b) t_{pp} , (c) $t_{pp\pi}$, and (d) t'_{pp} given in terms of electrons.

of the cation vacancy the holes in the anion valence p band feel a strong attraction to the vacancy site, and if large enough this attraction can bind two holes as in fact is found in the LDA calculations.

In order to get insight into the electronic structure of such an octahedral cluster of O^{2-} ions each with a full $2p$ shell we use a tight bindinglike molecular orbital (MO) approach. The symmetries of the MO's formed by the σ -bonding orbitals are a_{1g} , t_{1u} , and e_g at energies equal to $-4t_{pp} + \epsilon_\sigma$, ϵ_σ , and $2t_{pp} + \epsilon_\sigma$, respectively. Note that the simple sum of orbitals shown in Fig. 1(a) represents the a_{1g} symmetry state and this state has the lowest energy for electrons and the highest for holes. The π -bonding orbitals form the symmetries t_{2g} , t_{1u} , t_{2u} , and t_{1g} and have energies $-2t_{pp}$, $2t_{pp\pi}$, $-2t_{pp\pi}$, and $2t_{pp}$, respectively, where $t_{pp} = 1/2(t_{pp\sigma} - t_{pp\pi})$ with the σ and π hopping integrals now relative to the O-O bond direction and given in terms of electrons ($t_{pp\pi}$ is negative and $t_{pp\sigma} \sim -4t_{pp\pi}$). Note that for simplicity the zero of energy is chosen to be at ϵ_π . One can see that the irreducible representation t_{1u} appears in both the σ and the π combinations. As a result the molecular orbitals of only this particular symmetry will mix resulting in a shift of their energies to $1/2\epsilon_\sigma + t_{pp\pi} \pm 1/2\sqrt{(\epsilon_\sigma - 2t_{pp\pi})^2 + 32t_{pp}^2}$ for the MO formed by the σ ("+") and π ("-") bonding orbitals. The hopping integral t'_{pp} is defined as $1/2(t_{pp\sigma} + t_{pp\pi})$ as is clear from Fig. 1(d).

The schematic energy diagram is given in Fig. 2. The lowest energy states for holes are the e_g states formed by a linear combination of the p orbitals with lobes directed to the vacancy with phases such as to result in a e_g symmetry state when viewed from the vacancy and at the same energy the t_{1g} states with a corresponding linear combination of p orbitals with lobes directed perpendicular to the O-vacancy bond direction. A simple calculation shows

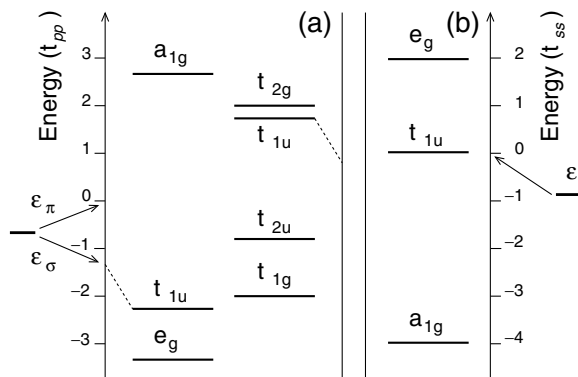


FIG. 2. Schematic single particle energy level diagram for (a) holes in anion orbitals and (b) electrons in cation orbitals. The dashed line in (a) represents a shift of energy levels of molecular orbitals with t_{1u} symmetry due to the mixture between σ - and π -bonding anion orbitals. The energies of the atomic σ and π orbitals are indicated by arrows in the left-hand margins.

that a hole in p orbitals with lobes pointing towards the vacancy has an energy about 1 eV lower than a hole in a p orbital with lobes perpendicular to the O-vacancy bond direction because of the crystal field produced by the effective $2-$ charge of the cation vacancy. Therefore the lowest energy single hole state will be the doubly degenerate e_g molecular orbital [Fig. 2(a)]. We note that this conclusion is independent of the parameters provided that $t_{pp\pi}$ is smaller in magnitude than $t_{pp\sigma}$ and the crystal field splitting is finite with $\epsilon_\sigma < \epsilon_\pi$ for holes. On the other hand for anion vacancies the conduction band orbitals of the cation would be occupied by the charge compensating electrons and their energy would be lowest for the non-degenerate a_{1g} orbital as also shown in Fig. 2(b).

Having understood the single-particle molecular orbitals, we move to the case of two holes (electrons) in the completely filled (empty) shell formed by the anion p (cation s) orbitals in the case of cation (anion) vacancies. If the Coulomb interaction between those particles is negligible, then two holes will occupy the e_g molecular orbital and they will form three degenerate states $1A_{1g}$, $1E_g$, and $3A_{2g}$ [Fig. 3(b)]. Two electrons on the other hand will result in a nondegenerate singlet ground state [Fig. 3(a)]. Let us now switch on the Coulomb repulsion of which the dominant term will be that when two particles are on the same site as in a Hubbard model. The three states found for the configuration with two holes will now split up because for the singlet states the two holes can be in the same site and in the same σ orbital

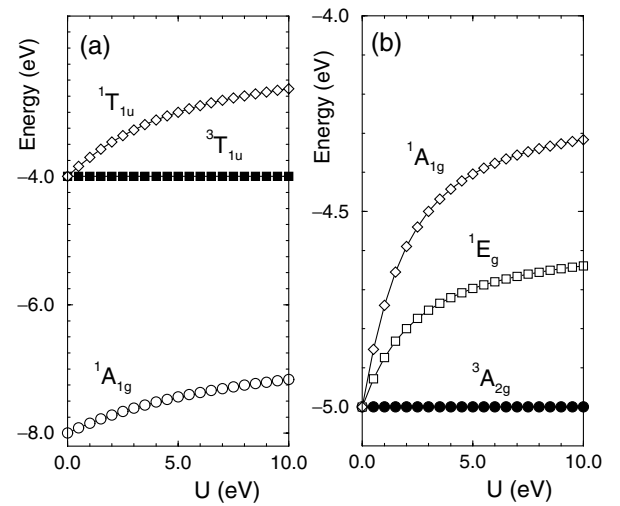


FIG. 3. Energy diagrams of the lowest three states for two particles in an octahedral cluster as a function of the on-site Coulomb repulsion U ; (a) two electrons introduced into the empty s orbitals with the hopping integral $t_{ss} = -1.0$ eV, and (b) two holes introduced into the completely filled p orbitals with the hopping integrals $t_{pp\sigma} = 1.2$ eV and $t_{pp\pi} = -0.3$ eV and the crystal field potential $\epsilon_\sigma = 1$ eV and $\epsilon_\pi = 0$ eV given in terms of electrons. Solid (open) symbols are for spin triplet (singlet) states.

while this is forbidden for the spin triplet state. This means that the singlets will increase in energy leaving us with a triplet and magnetic ground state. From Auger spectroscopy studies of a large number of simple oxides the on-site Coulomb repulsion energy of two holes in an oxygen p orbital is 5–7 eV [8,9].

To shed more light on this issue we carried out exact diagonalization calculations for the single octahedral cluster with two electrons in s orbitals as well as with two holes in the p orbitals of a octahedral cluster taking into account the on-site Coulomb interaction U exactly, and the results are shown in Fig. 3. One can immediately see that while a spin singlet state is the ground state for two *electrons* independent of the value of U , a spin triplet state is the ground state for the two *holes* as soon as U is different from zero. This triplet state has symmetry $3A_{2g}$ and the wave function consists mainly of a $(e_g)^2$ configuration shown schematically in Fig. 2(a). Note that the lowest singlet state is at about 0.3–0.4 eV higher in energy than the triplet ground state of the two holes for realistic parameters. As mentioned above this is a kind of molecular Hund's rule coupling and is a result of the degenerate nature of the lowest energy molecular orbital for holes in a octahedral cluster. We note that for oxygen vacancies it does not matter if we are dealing with s or p states of the cations. As long as the band is empty the lowest energy state for electrons in octahedral geometry will always be a totally symmetric state and therefore nondegenerate.

Now that we have found that cation vacancies in simple divalent monoxides with the rock salt structure or in general cation vacancies in compounds with octahedral coordination form impurity states with local magnetic moments, we may ask what the magnetic state of the material is for a finite concentration of such vacancies. Do they couple ferromagnetically or antiferromagnetically and is the resulting material metallic or still insulating? To address this we consider a super lattice of cation vacancies with a $2 \times 2 \times 2$ supercell. This would correspond to a vacancy concentration of only 3.125%. We calculate the electronic structure using a density functional band structure code (TBLMTO-47 [10]) based on the LDA. As a basis we used $4s$, $4p$, and $3d$ orbitals on Ca $2s$, $2p$, and $3d$ orbitals on O and $1s$, $2p$, and $3d$ orbitals on the empty spheres.

Before we discuss the results of the band structure calculations we note that, due to the ionic character of this compound, the valence band is formed of mainly oxygen $2p$ orbitals and is full, and the conduction band is formed of mainly Ca orbitals and is empty. Pure CaO is therefore a diamagnetic insulator with a calculated band gap of 3.46 eV. The experimental gap is 7 eV [11].

In Fig. 4 we observe the impurity state just below the conduction band and the chemical potential shifted up above this impurity state for oxygen vacancies. This material is a nonmagnetic metal. The same calculation for MgO with oxygen vacancies exhibits a clear gap separat-

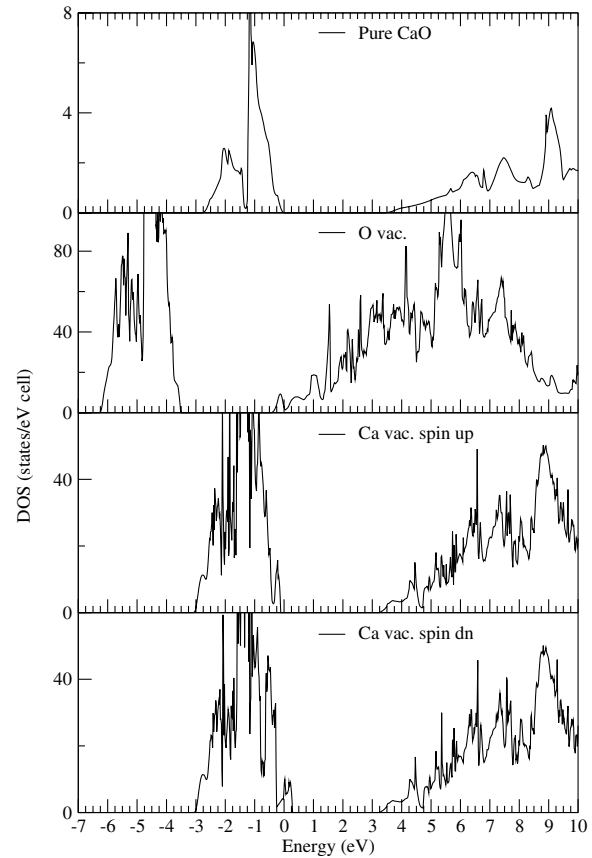


FIG. 4. Total density of states of pure CaO (upper panel) and with 3.125% anion (second panel) and cation (two lower panels) vacancies. The zero of energy is at Fermi energy.

ing the defect induced band from the conduction band resulting in an insulating nonmagnetic ground state.

In sharp contrast the band structure for Ca vacancies exhibits also well-defined defect state bands crossing the Fermi energy resulting in a metallic solution. Also here we see the clear split off character of the vacancy induced states consistent with the physical picture we presented above of the effects of the defect potential. Even more interesting is the fact that the Ca vacancy material is found to be ferromagnetic and the bands crossing the Fermi energy are totally spin polarized. A Ca deficiency results in a magnetic moment of $2\mu_B$ per supercell, 88% of which is concentrated on the six oxygen ions that are the nearest neighbors to the Ca vacancy.

In both cases of Ca or oxygen vacancies we find that the charge compensating holes or electrons are rather strongly bound to the vacancy. In Figs. 5 and 6 we show the partial density of states projected on the impurity site. It is easy to see that in the case of Ca vacancies the holes are mainly d like, formed primarily from a linear combination of oxygen p orbitals on neighboring sites with e_g symmetry. Band structure effects also introduce quite a strong component of p symmetry at the Fermi energy. The result is a half-metallic ferromagnet. On the other

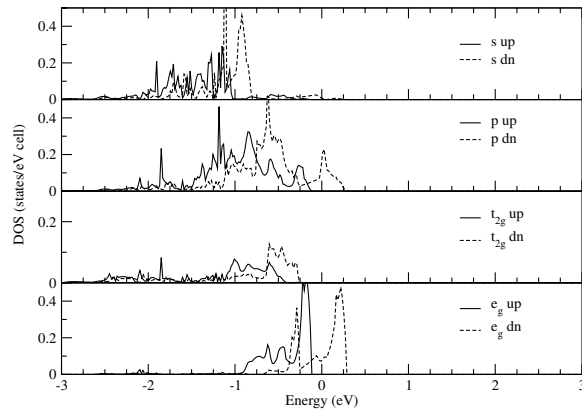


FIG. 5. Ca vacancy partial density of states. The zero of energy is at Fermi energy.

hand, electrons induced by oxygen vacancies occupy local molecular orbitals of s symmetry and result in a non-magnetic ground state. Both of these agree very well with the results of our cluster calculations. We suggest that the picture presented describes a path to new classes of magnetic materials and is a very general phenomenon.

The general underlying rule for obtaining a magnetic ground state is that the crystal structure must be such that the ground state of the charge compensating molecular orbital is orbitally degenerate. Secondly the local impurity potential should be large enough to quite strongly bind the charge to the nearest neighbor atoms which is needed to validate the treatment as a cluster or molecule which then will result in the formation of a local moment. An on-site Coulomb interaction will then result in a high spin ground state for more than one electron or hole in such a molecular orbital which will mediate a ferromagnetic magnetic coupling between such clusters via either a superexchange or a double exchange-like mechanism. We note that for the case considered above the charge compensating clusters have considerable overlap even though the concentration is only a few per cent. We also note that such degenerate ground states are common for high symmetry systems such as ringlike structures in addition to the octahedron considered here.

In conclusion we have demonstrated that point structural defects in crystals such as vacancies can indeed confine the compensating charges in molecular orbitals formed by atomic orbitals on the nearest neighbors. We have shown that under certain conditions local magnetic moments will be formed due to a kind of molecular Hund's rule coupling with energetics determined by kinetic energy and symmetry considerations rather than

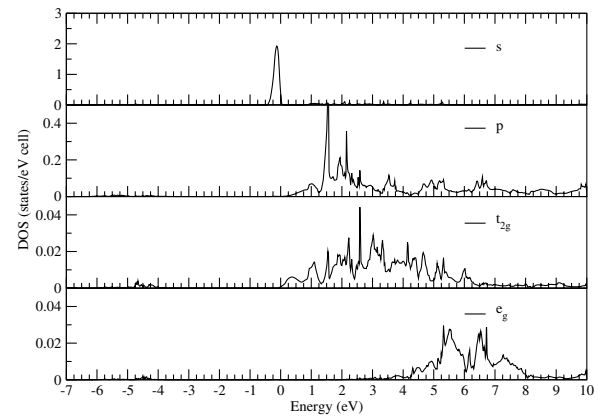


FIG. 6. Density of states projected onto the O vacancy site. The zero of energy is at Fermi energy.

exchange interactions. This can lead to ferromagnetic ground states and in the example discussed even a half-metallic ferromagnetic ground state. The actual Curie temperature is difficult to estimate but if the majority spin/minority spin splitting is anywhere near to an indication of the ordering temperature we expect it to be very high. Theoretical studies are in progress using LDA + U and the method described by Lichtenstein [12] to determine the intercluster exchange interaction. Because of the rather general nature of the physics presented we believe that it may describe a path towards a new class of ferromagnetic materials.

-
- [1] D. P. Young *et al.*, Nature (London) **397**, 412 (1999).
 - [2] Y. Matsumoto *et al.*, Science **291**, 854 (2001).
 - [3] K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001).
 - [4] R. Monnier and B. Delley, Phys. Rev. Lett. **87**, 157204 (2001).
 - [5] H. C. Longuet-Higgins, J. Chem. Phys. **18**, 265 (1950).
 - [6] J. B. Torrance *et al.*, J. Appl. Phys. **63**, 2962 (1988).
 - [7] H. Eskes, Ph.D. thesis, University of Groningen, 1992.
 - [8] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, Phys. Rev. B **38**, 11 322 (1988).
 - [9] S. Altieri, Ph.D. thesis, University of Groningen, 1999.
 - [10] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
 - [11] R. C. Whited and W. C. Walker, Phys. Rev. **188**, 1380 (1969).
 - [12] A. I. Lichtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, J. Magn. Magn. Mater. **67**, 65 (1987); A. I. Lichtenstein *et al.* Phys. Rev. B **52**, R5467 (1995).