

**Zinc-blende CaP, CaAs and CaSb as half-metals: A new route to magnetism in calcium compounds**

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Existence of ferromagnetism in bulk calcium compounds is discovered theoretically. First-principles calculations of calcium phosphide, calcium arsenide and calcium antimonide in the zinc-blende structure have been performed to show the half-metallic ground state in each optimized stable structure. Magnetism comes from spin-polarization of electrons in p-orbitals of P, As or Sb and d-orbitals of calcium atoms. The half-metallicity is analogous to the half-metallic zinc-blende compounds, e.g. CrAs or CrSb, but the predicted compounds become ferromagnetic without transition metals. In (In1−xCa)xSb, the magnetism remains to be stable in a range of the doping rate (x > 0.8).

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In recent progress of spin electronics, discovery of novel magnetic materials accelerates researches in this rapidly progressing field. Almost complete search for possible transition metal doping into III-V semiconductors or II-VI compounds. In addition to the dilute magnetic semiconductors (DMS), new classes of materials were discovered as end materials of the doping. For the case of Mn-doping into GaAs, denser doping is not easy, but the theoretical calculation of the end material i.e. MnAs in the zinc-blende structure, shows that the material should be a half-metal. For the case of Cr-doping into GaAs or InSb, end materials are known to possess the half-metallic band structures by the first-principles calculations. Several ferromagnetic materials including zinc-blende CrAs (zb-CrAs) and zb-CrSb were indeed successfully synthesized based on the recent theoretical prediction.

An interesting trend in the list of DMS obtained by doping of every possible transition metal element is that the strong magnetism is realized when the d-shell is partially occupied by electrons and is not half-filled. Cr or Mn in GaAs and Co in ZnO seem to be optimal for the half-metallicity. Fe, Co, Ni are not necessarily suitable for the dopant. We would be able to obtain a better and deeper understanding of the magnetic effect in these curious materials by looking at all possible compounds including magnetic semiconductors.

In this paper we report on first-principles electronic structure calculations of calcium compounds i.e. CaX (X= P, As and Sb). These materials are supposed to form the zinc-blende structure. In these crystals, the most interesting character of the band structure is that the highest occupied band becomes almost dispersion-less. This curious flat band, which creates a sharp peak in the density of states (DOS) at the Fermi level, originates from hybridization of p-orbitals of pnictides and Ca 3d orbitals. In this p-d hybridized band, ferromagnetism arises. Indeed, our spin-dependent generalized-gradient-approximation (spin-GGA) calculation reveals that calcium phosphide, calcium arsenide and calcium antimonide in the zinc-blende structure (zb-CaP, zb-CaAs and zb-CaSb in short) possess half-metallic band structures.

So far, several Ca compounds were discussed as possible ferromagnetic materials. In CaB6, the ferromagnetism reported in the literature was argued as a defect-mediated spin-polarization. B6 vacancies were supposed to be an origin of magnetism. Inter-orbital exchange interactions between degenerate molecular orbitals in a B62− cluster could be large enough to cause ferromagnetic behavior. Similar argument was proposed for CaO in the rock salt structure. The mechanism was derived from consideration of possible attraction between two holes in doubly degenerate molecular orbitals on a cluster of O2− surrounding a Ca vacancy. Since the exchange interaction between holes would be ferromagnetic, there could be formation of a triplet state at the cluster, which was essential for the argument. Thus, in these examples, the magnetism was supposed to be favored due to degenerate orbitals on anion clusters but not on orbitals of Ca.

In the case of zb-CaX, as shown in the following discussion, orbitals on calcium atoms play essential roles for the magnetism. Thus our finding of half-metallicity appearing in the zinc-blende Ca compounds is new. Here it might be meaningful to comment the superconductivity found in a high pressure phase of Ca, since d-orbitals play important roles. Existence of d-orbitals induced by the crystal field at Ca sites are not rare. Some theoretical studies of d-orbitals of Ca and/or alkaline earth elements and divalent rare earth elements, are found in the literature.

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TABLE I: The optimized lattice constants of zb-CaP, zb-CaAs and zb-CaSb obtained by the spin-GGA calculation for the ferromagnetic states. The lattice constant of InSb determined by an experiment as well as an optimized value by the calculation is shown for comparison.

| Material | Lattice constant [Å] |
|----------|----------------------|
| zb-CaP   | 6.55, 6.75           |
| zb-CaAs  | 7.22, 6.65           |
| zb-CaSb  | 6.48 [20]            |
| InSb(Exp)|                      |

The first-principles band-structure calculations to determine the electronic structure were done for each material by adopting the spin-GGA as the exchange-correlation energy functional. The full-potential linearized augmented plane wave (FLAPW) method was utilized. All of the numerical calculations with this method have been done using the Wien2k code. The lattice constant, the electronic structures and the magnetic moments, accurately, except for overestimation of the lattice constants caused by the spin-GGA calculation. For InSb the present calculation overestimates the lattice constant by 2.6 % as shown in Table I. To investigate the case of Ca-doped compounds we have used a Korringa-Kohn-Rostker method combined with a coherent potential approximation (KKR-CPA) based on a local density approximation. The form of the potential was restricted to the MT type. The wavefunctions in the MT sphere were expanded in spherical waves with the angular momenta up to $l_{\text{max}} = 10$. The criterion of the energy convergence is set to 0.001 mRy and we have as well checked the charge distance between the last two iterations and that has converged less than 0.0001. Five hundred k-points are taken in the first Brillouin zone. Our calculational conditions are enough to determine the lattice constant, the electronic structures and the magnetic moments, accurately.

We now discuss details of the electronic structure of zb-CaAs as a typical example. The DOS of zb-CaAs is shown in Fig. 2. The valence band is strongly spin polarized with the exchange splitting of ~ 0.6 eV. A sharp peak is found at the top of the valence band. The Fermi level locates at the peak of the minority-spin band. A gap opens in the majority-spin band and the present system is the half-metal. The origin of the curious peak of the DOS is an almost dispersionless band. (Fig. 2) More precisely, a spin-down flat band forming the peak is empty, while a spin-up flat band is filled by electrons. We can clearly see $d$-components of Ca in this dispersionless band. (See Fig. 2) Although the valence band is almost composed of $4p$-orbitals of As, the dispersion of the top band is determined by the $p-d$ hybridization. Note that $p$ bands become dispersive if As atoms are supposed to form an FCC structure with the same lattice constant.

To understand the magnetism, we specify characters of $d$-components of Ca in the band structure of zb-CaX. Following the ligand field theory, we see that degenerate $d$-orbitals are split into two levels in a crystal field with the tetrahedral symmetry. The $d\gamma$ level becomes the lower level and the $d\xi$ level becomes the upper one. The present result, of course, follows this rule and $d\gamma$ and $d\xi$ levels are at about 4.0 eV and 5.0 eV in the conduction band, which is shown in the partial DOS (Fig. 2). Now the $d$-components appearing in the vicinity of the Fermi level is $d\xi$. (Fig. 2) This is because $d\xi$ orbitals are strongly hybridized with $p$-components of As. Formation of bonds is due to this $p-d$ hybridization in the zinc-blende structure. This $p-d$ hybridization is often seen in magnetic compounds in the zinc-blende structure. Thus electrons prefer to occupy $d\xi$ orbitals rather than to do $s$-orbital or $d\gamma$. The peak of the $d\xi$ component in the vicinity of the Fermi level is not caused by the crystal field, but caused by the bond formation. These characteristics are common in zb-CaX.
Because pnictide elements form a framework of the zinc-blende structure via $p$-$d$ hybridization, the valence band structure of zb-CaX is basically similar to a series of compounds composed of $3d$ transition metals and $V$ elements and/or VI elements. We now discuss similarity and difference between zb-CaX and other compounds.

The amount of the magnetic moment depends on occupation of electrons in the $d$ levels. For the conventional transition metal compounds, for example, the magnetic moment of MnAs is $4 \mu_B$. Valence electrons are twelve ($3d^5$ $4s^2$ from Mn and $4s^2$ $4p^3$ from As) per a chemical formula. However, two $4s$ electrons of As are in quite deep energy levels at about -10 eV and these levels do not contribute to the bond formation and magnetism. The rest ten electrons contribute to them. Six of those electrons contribute to bond formation and four of them occupy $d$ levels and contribute to magnetism.

With replacing Mn to Cr, V, Ti, and Sc, the magnetic moment per a transition metal atom decreases as 3, 2, 1, 0 $\mu_B$, respectively. Because of Hund’s rule coupling, spins of electrons occupying $d$ levels are parallel in each atom. These high spin states are ferromagnetically aligned via the double exchange mechanism or by the $p$-$d$ exchange mechanism depending on the resulting electronic structure. This is the origin of magnetism of transition metal pnictides or chalcogenides with the zinc-blende structure.

In zb-CaAs, five electrons ($4s^2$ of Ca and $4p^3$ of As) contribute to bond formation and magnetism. Since one electron per a chemical formula is missing to fill the valence $p$ bands, a hole band appears. Interestingly, at the top of the valence band, $d$ character is enhanced and the band becomes very flat. This fact suggests that interference effect occurs to make a localized orbital per an As atom. Thus, localized nature appears at the top of the band. The Fermi level comes just at this band and rather large exchange splitting appears due to the high DOS. As well as GaAs, the bonds of zb-CaAs are not strong covalent bonds and they do not suppress magnetism.

In zb-CaAs, however, there is no localized $d$ spins. Actually, polarized band is $p$ bands slightly hybridized with $d$-orbitals of Ca. There is no room for the double exchange nor for the $p$-$d$ exchange to work. The magnetism should be understood by another mechanism. The DOS of these curious $p$-$d$ hybridized bands looks like that of Ni where the Fermi level comes at a peak position of the DOS. This is favorable for itinerant mechanism of ferromagnetic ordering. Here, it is worth commenting that the dispersionless band is just half-filled. This situation is rather similar to the flat-band ferromagnetism.

The magnetic moments of zb-CaX are shown in Table II. In all cases the total magnetic moment is 1 $\mu_B$. Ca has only the tiny magnetic moment and P, As and Sb do have the moments. A large amount of the moment is found in the interstitial region. The moments in the

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**TABLE II:** The magnetic moments of zb-CaP, zb-CaAs and zb-CaSb obtained by the spin-GGA calculation. Those of Ca and X are defined in the MT spheres. Interstitial represents an amount of the magnetic moment in the interstitial region.

| Compound | Total | Ca | X |
|----------|-------|----|----|
| zb-CaP   | 1.000 | 0.092 | 0.511 |
| zb-CaAs  | 1.000 | 0.110 | 0.459 |
| zb-CaSb  | 1.000 | 0.139 | 0.369 |

**Interstitial:**

| | 0.397 | 0.431 | 0.492 |

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**FIG. 2:** The DOS of zb-CaAs. The upper panel shows the total DOS, while the middle and lower represent the partial DOS decomposed into $4p$-components of As, $3s$, $3p$- and $3d$-components of Ca plotted in the broken, dotted and solid lines, respectively, and decomposed into $dx$ and $dy$ states of Ca plotted in the broken dotted and solid lines in the lower panel, respectively.

**FIG. 3:** The electronic band structure of the zb-CaAs. The left and right panels are spin-up and spin-down components, respectively.
We now investigate magnetism in Ca-doped compounds, (In$_{1-x}$Ca$_x$)Sb. The electronic states have been calculated by the KKR-CPA method. In this calculation the experimental lattice constant (6.48 Å) is used. As shown in Fig. 4 the magnetic moment appears at about 80% of the doping rate and it increases monotonously to about 1 $\mu_B$. We checked the DOS profile for each doping rate. The sharp peak of the DOS originated from the dispersionless band appears from low doping rate and it moves upward on the energy axis with increasing doping rate. When the peak comes just at the Fermi level, the magnetic moment appears.

We have shown theoretically that Ca compounds in the zinc-blende structure show ferromagnetism. The spin polarization occurs due to the exchange interaction in $p$-$d$ hybridized bands. The localized nature of the electronic states appears as a polarized flat band at the top of the valence band. The half-metallic calcium compounds without the transition metals may open new applications in spin electronics in addition to better understanding of ferromagnetism found in several zinc-blende compounds.

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FIG. 4: The magnetic moment per a chemical formula as a function of Ca-doping rate in (In$_{1-x}$Ca$_x$)Sb. Ca atoms substitute In sites.