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New half-metallic materials with an alkaline earth element

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Abstract

New candidates for half-metallic materials were theoretically designed recently by Geshi *et al*. The materials are calcium pnictides, i.e. CaP, CaAs and CaSb. When the zinc-blende structure was assumed, these compounds showed half-metallic electronic band-structure, in which a curious flat band was found. To explain this magnetism, we investigated characters of orbitals on this flat band of CaAs. The hybridization of p states of As with d states of Ca is shown to be essential for formation of a flat band made of localized orbitals. The appearance of complete spin polarization in the flat band suggests that the flat-band mechanism is relevant for the ferromagnetism. A connection from the first-principles result to a solvable Hubbard model with a flat band is discussed.

1. Introduction

Very recently, a series of novel magnets was theoretically designed [1]. The materials are compounds of calcium and group V elements. In this first report, the zinc-blende (zb) structure was assumed for these compounds. The lattice constants were determined with cubic symmetry fixed. Interestingly, bulk ferromagnetism was confirmed by a first-principles calculation using FLAPW [2] with the spin-GGA energy functional [3]. The electronic band structure shows half-metallicity with a spin moment of almost 1 μ_B per Ca atom. The result was confirmed by other calculations with the KKR method [4] and the plane-wave expansion utilizing the ultra-soft pseudo-potential [5, 6].

The magnetism arises without transition-metal elements. This is a remarkable characteristic of these compounds. Actually, the obtained density of states shows that the spin polarization occurs in the p bands of the pnictides [1]. Thus these materials may be examples of p-band ferromagnets which are rarely seen except for organic magnets and the recent theoretically designed doped CaO [7].

After the first report, stability of the zinc-blende structure was tested [8]. Comparing to the known CaAs structure, for example, zb-CaAs is energetically unstable. Besides, there is

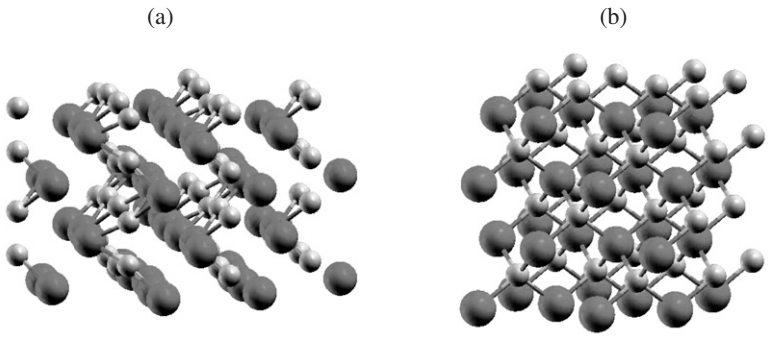

Figure 1. (a) The CaAs structure and (b) the zinc-blende structure. Although the latter structure is a saddle-point of the potential energy surface of CaAs, we consider the structure to discuss the magnetic property of the material.

no energy barrier against the lattice distortion and tetragonal distortion was shown to occur. The zinc-blende structure itself is a saddle-point structure. However, the magnetism remains in a distorted meta-stable solution. Besides, lattice distortion may be controlled by creating this structure as a thin film on an appropriate substrate. Moreover, to understand origin of the curious p-electron ferromagnets, we may consider the zinc-blende calcium pnictides as ideal materials for theoretical analysis.

In the band structure of zb-CaAs, there appears an almost dispersionless band at the top of the valence band [1]. Thus the density of states shows a sharp peak in both majority and minority bands. The band splits with exchange splitting of about 0.6 eV. The Fermi level locates at this curious band which is empty for the minority spins. On the other hand, the majority band has a gap above this flat band. The system is thus a half metal but with a gap in the majority band. This is in contrast to similar half-metals like CrAs and CrSb, where the majority spins are metallic and a gap opens for the minority band [9, 10].

In this paper, we analyse the electronic state of zb-CaAs to explore the magnetic mechanism in this material. The flat band is made by hybridization of p orbitals in group V atoms and Ca 3d orbitals induced by the crystal field. We will show that the occurrence of the flat band is due to an interference effect. By looking at the density of states, we conclude that the flat band for spin-up electrons is filled, while that for spin-down electrons is empty. Thus, the flat band is just half-filled in this system. We will conclude that the so-called flat-band ferromagnetism found in the Hubbard model [11] is relevant for the understanding of the magnetism of zb-CaAs. To show a direct relation with the flat-band ferromagnetism, we will give a strategy to explain the ferromagnetic mechanism. Part of the theoretical process has been completed. Several properties due to the flat-band ferromagnetism are also discussed.

2. Structure and magnetic solution of zb-CaAs

CaAs is one of the inter-metallic compounds made of a strong cationic metal and a weak anionic metal, which are known as the Zintl phase. Thus, the valence of Ca is almost +2 while the As have two extra electrons each. The lattice structure of CaAs known in the literature belongs to the space group $P\bar{6}2m$ (figure 1(a)). This structure does not show magnetism.

In the previous paper [1], we considered the zinc-blende structure instead (figure 1(b)). The motivation was to find an analogue of half-metallic transition metal pnictides. Since Ca has a rather large ionic radius, the lattice constant becomes large. The theoretically optimized value is 6.75 Å, when the zinc-blende structure is assumed.

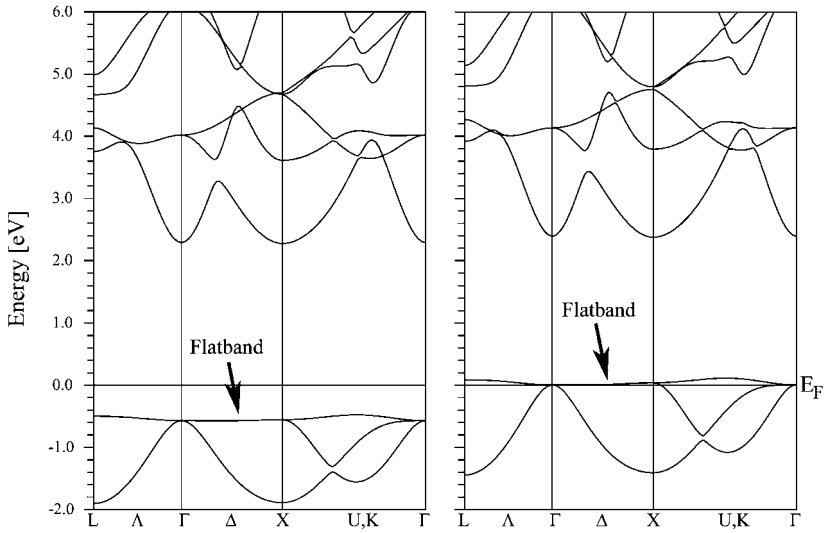

Figure 2. The electronic band structure of the zb-CaAs. The left and right figures show that of spin-up electrons and spin-down electrons, respectively. We can see the flat band in both band structures. For the minority spin, the flat band is empty.

The electronic band structure was obtained for zb-CaAs using the spin-GGA (figure 2). The FLAPW method was utilized. Calculational conditions are described in the previous paper [1]. The valence band is the As 4p band. Five electrons per formula unit of CaAs fill the bands. Thus the highest valence band becomes half filled.

We can see the existence of a flat band in the whole Brillouin zone. In this magnetic solution, the flat band for the minority spin is empty. Thus the total magnetic moment becomes $1\,\mu_B$ per CaAs. The band splits with a finite exchange splitting of $\sim$0.6 eV, which is independent of the wavenumber. This feature is a characteristic of a strong magnetism always found in the flat-band ferromagnetism in the Hubbard model with 100% spin polarization of the band. This feature itself tells us that the flat band consists of strongly localized orbitals.

To have this special band structure, selection of Ca seems to be very important. One reason is the number of valence electrons. When a di-valent cation is selected, the p bands of the pnictogen are doped to give the half-filled flat band. Another reason is that orbitals of Ca create the flat band as discussed in the next section.

3. Flat-band mechanism in CaAs

In this section, we discuss the possible flat-band mechanism, which would be relevant for the ferromagnetism in CaAs. We first show that origin of the flat band is an interference effect between p orbitals of As and d orbitals of Ca. Next, we will address an approach to show the ferromagnetic mechanism by using known argument on theoretical models.

3.1. Origin of the flat band

To show that origin of the dispersionless band is an interference effect, we compare the band structure of the magnetic solution with that of the non-magnetic solution and another band structure made up by As only. In figure 3(a), the flat band appears at the Fermi level. The

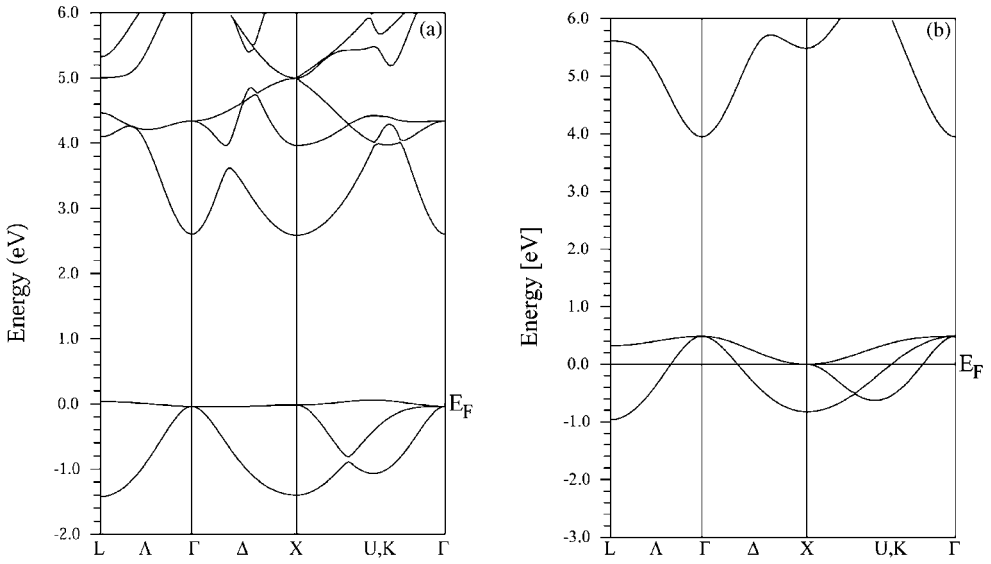

Figure 3. (a) The band structure of paramagnetic zb-CaAs. (b) The band structure of hypothetical As in the FCC structure. The lattice constant is the same as that of zb-CaAs.

flatness is almost the same as the magnetic solution (figure 2). Thus, formation of the flat band is purely due to the structure of the bond connection between atomic orbitals on As and Ca. To show the importance of Ca, we consider an FCC lattice structure of As with the lattice constant of zb-CaAs. In this band structure (figure 3(b)), As p bands have dispersive branches only. The topmost band of the p bands is not flat. Therefore, the flatness of the curious p bands arises from a special structure in the atomic orbitals of zb-CaAs, which causes an interference effect to make some p-origin orbitals very localized.

We have obtained the same flat band using the conventional tight-binding model [12]. Important ingredients are Ca d_ε orbitals. Actually, by artificially controlling strength of transfer integrals between each pair of an As orbital and a Ca orbital, we have checked that relevance interference occurs by the p–d_ε mixing. However, we should note that the final isolated p bands including the flat band are constructed only when As 4s and 4p orbitals and Ca 4s, 4p and 3d orbitals are hybridized.

3.2. A scheme to show the flat-band ferromagnetism in CaAs

To understand magnetism, we may often utilize a simplified effective model, which is relevant for description of the physics in a low energy scale. The band structure calculation offers a nice starting point which selects a good basis (Kohn–Sham orbitals) from general bases like the plane-wave basis which has high energy states at a few tens of Ryd or much higher energy. By using this set of orbitals, the exchange is evaluated using the exchange–correlation functional in the density functional theory. However, this description is not always enough for better understanding of the magnetism. Thus we would like to make some connection between a correlated electron model and the result of the DFT-GGA calculation and utilize knowledge on the solvable model.

In the present case, we can consider an approach which may give a well defined method to make a continuous connection between the ground state of DFT-GGA and that of the Hubbard

model. The similarity of the DFT-GGA band and the tight-binding band suggests that reduction of the phase space of single-particle orbitals is possible up to that spanned by the atomic orbitals considered here. We can optimize the transfer integrals in the tight-binding model to adjust the band structure of zb-CaAs. We call the obtained model model I, which is made from 13 atomic orbitals of CaAs. By obtaining the Wannier orbital of the nearly flat band, we have almost localized orbitals. To construct the flat-band model, however, we need a completely flat band. This is obtained by constructing the tight-binding model with a strictly localized orbital [13]. We call the latter model model II. Model I and model II are interconnected by change in the transfer integrals. For model II, we have a proof of ferromagnetism, although it is a perturbative description allowable only for small U [11, 13].

Now, we consider adiabatic connection of the ferromagnetic solution of models. For model I, a ferromagnetic state can be found by introduction of inter-electron interactions and by the mean-field approach. To have a connection between a DFT-GGA solution in the Kohn–Sham description and any solution of the Hubbard model, we may be required to introduce a single-particle description for the Hubbard model by some approximation, since the unpolarized valence bands would be qualitatively different if we treated the Hubbard Hamiltonian accurately. Thus, we consider an approximation here. The phase diagram of the Hubbard model including models I and II has to be explored. The naive expectation at this stage is that since model I has a nearly flat band the ferromagnetic phase is connected when the Hubbard interaction U is large enough. However, this part requires careful analysis, because we may have a phase transition for large U. If the ferromagnetic phase is connected, we should finally show that the mean-field phase diagram is quantitatively correct for models I and II in a required range of U. This scheme, however, has its own difficulties. By the inclusion of a mean-field approach, we cannot judge whether a phase transition in the Hubbard model occurs during connection or not.

If we wish to know the nature of the material, we may have find another method. The DFT-GGA calculation concludes in ferromagnetism for zb-CaAs. In the electronic structure, we have found that (1) the interference effect makes a flat band, (2) the flat band is half-filled and (3) a full spin-polarization occurs in the flat band. Since these characteristics are generally found in the flat-band ferromagnetism in the Hubbard model when half-filled, we may define flat-band ferromagnetism in DFT-GGA calculations as the occurrence of a ferromagnetic solution satisfying these three conditions.

4. Summary and conclusion

We have discussed the ferromagnetic ground state of CaAs found in the first-principles calculation. If we look only at the stable structure, the magnetic mechanism might be concluded to be Stoner-type ferromagnetism due to exchange in itinerant electrons. However, the strange behaviour in this p-electron system would not be clarified sufficiently. In the present case, since we have a special feature, i.e. the flat band already in the DFT-GGA band structure, we can understand the reason for the magnetism. To confirm the mechanism more accurately, we need to show a direct connection between the obtained DFT-GGA result and the theory of the Hubbard model by a method given in the last section, which is left for future discussion.

Although the stable structure of CaAs with ferromagnetism is possibly a distorted zinc-blende structure, we may consider the properties of CaAs as a flat-band ferromagnet. Since a nearly flat band exists near the Fermi level, the electric conductivity is not high. Besides, As 4p electrons create the magnetic moments. Thus conduction and magnetic properties would be similar to those of organic magnets, where 2p electrons take part in the magnetism. In these p-electron magnets, bond connection or network paths of electron transfer are decisive for

the magnetism. Interestingly, similarity is seen as a realization of flat-band ferromagnetism. For these p-electron materials, we may have much room for materials design, where network topology of p (or π) orbitals should be a guiding principle.

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