Lattice and magnetism in superconducting compounds $Ca_{1-x}K_xFe_2As_2$*

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Based on the density functional theory (DFT), using the scheme of the linearized augmented plane wave and the improved local orbital (APW + lo), the structure, the electronic bands and the magnetism of superconducting compounds $Ca_{1-x}K_xFe_2As_2$ (x = 0, 0.25, 0.5, 0.75, 1) are optimized and calculated. The calculation results indicate that with K-doping the lengths of the a, b axes can decrease, and the length of the c axis, the volume, the energy of spin-down valence bands, and the DOS at the Fermi level can increase, which leads the magnetic moment of the system to increase.

Keywords: $Ca_{1-x}K_xFe_2As_2$, density functional theory (DFT), lattice, magnetic moment.
PACC: 7470H, 7430J, 7120H

1. Introduction

The recent discovery of superconductivity in doped iron arsenide compounds[1−3] and the later improvement on the superconducting transition temperature T_c in pnictide oxides RFeAsO$_{1-x}$F$_x$ (where R = La, Nd, Sm, Pr, ...) (R1111)[4−7] and the $ThCr_2Si_2$-structure compounds $A_{1-x}B_xFe_2As_2$ (A = Ba, Sr, Ca, B = K, Cs, Na) have caused extensive experimental and theoretical studies of this new kind of material with layered FeAs planes. Understanding the physics of superconductivity in high-T_c layered FeAs compounds and other unconventional superconductors remains a central unresolved problem at the forefront of condensed matter physics. One widespread school of thought maintains that in both R1111 and AFe_2As_2, magnetic fluctuations are intimately involved in the pairing mechanism. It is interesting that a spin-density wave (SDW) and the transition from high-temperature tetragonal structure to low-temperature orthorhombic structure take place simultaneously above 100 K.[8−11] Superconductivity in the AFe_2As_2 family can be induced by either electronic/hole doping on the A site or by applying a pressure. Boeri *et al.* predicted[12] a negligible contribution of the weak electron–phonon to the superconductivity for $CaFe_2As_2$ by using DFT calculations. It is shown by Kurmaev *et al.*[13] based upon their DFT calculation and x-ray spectra that the Fe 3d-states dominate at the Fermi level of $CaFe_2As_2$.

Clearly, the understanding of electronic, magnetic, and structural properties of the parent FeAs compound is the key to determining the underlying mechanism that makes these materials superconductive upon electron/hole doping. In this paper we present a detailed first-principles study of K-doping AFe_2As_2 with the main focus on lattice, magnetism, and electronic structure. The effect of K-doping is also discussed.

2. Method

The linearized augmented plane wave (LAPW) method is one of the most accurate methods of calculating electronic structures of crystals. It is based on the density functional theory (DFT) for the treatment of exchange and correlation and the use of e.g. the generalized gradient approximation (GGA). Like

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most energy-band methods, the LAPW method is a procedure for solving the Kohn–Sham equations for the ground state density, total energy, and eigenvalues (energy bands). In the procedure, every unit cell volume is partitioned into two regions: non-overlapping muffin-tin spheres around each atom and the remaining interstitial area. Two different sets of basis functions are used in the two regions. For the wave functions inside the atomic sphere a linear combination of radial functions that are time spherical harmonics and in the interstitial region a plane wave expansion are used. In order to increase the flexibility of the basis and to make possible a consistent treatment of semicore and valence states in one energy window, additional basis functions (local orbitals (LOs)) are added. Sjöstedt, Nordstrom, and Singh[14] have shown that the standard LAPW method with the additional constraint on the plane waves (PWs) of matching in value and slope to the solution inside the sphere is not the most effective way. They suggested a new scheme with improved local orbitals (denoted as lo to distinguish from the standard LO), which does not require the wave functions to be smooth at the sphere boundary. Madsen *et al.*[15] have shown that the new scheme (denoted as APW + lo) converges practically to identical results to the standard LAPW, but leads to significantly smaller basis sets and less computational time.

In the present paper, the calculations are performed within the framework of DFT implemented in the WIEN2K code,[16] by using the APW+lo scheme with the exchange–correlation potential based on the Perdew, Burke, and Ernzerhof (PBE) formalism of GGA. The energy cutoff for the plane wave expansion of the wave function in the interstitial region is chosen to be –6.0 Ryd. A muffin-tin radius of 2.0 a.u. is used for Ca, K, Fe, As atoms separately, and a mesh of 300 k points is generated in the irreducible wedge of the Brillouin zone.

3. Results and discussion

3.1. Crystal structure

A plate-like single crystal of $CaFe_2As_2$, which crystallizes in the $ThCr_2Si_2$ tetragonal structure, is shown in Fig. 1. The layers of edge sharing Fe4As4-tetrahedra are separated by Ca atom layers shown in experiment[17] with a sharp transition between the tetragonal and orthorhombic structures at TS 172.5 K–173.5 K. For the body-centre tetragonal structure, the space group is $I4/mmm$, the crystal unit shown in Fig. 1 involves four primitive cells with $a = b$; and for the face-centre orthorhombic structure, $Fmmm$, Fig. 1 involves two primitive cells with $a \neq b$.

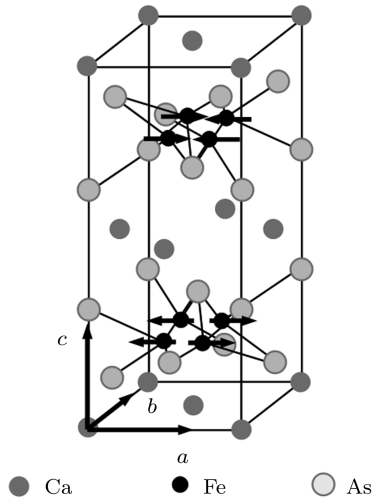


Fig. 1. Crystal structure of $CaFe_2As_2$.

The lattice constants of $Ca_{1-x}K_xFe_2As_2$ ($x = 0$–1) are optimized and listed in Table 1.

Table 1. Lattice constants.

		this work			
	space group	a/nm	b/nm	c/nm	V/(nm^3/f.u.)*
$CaFe_2As_2$	$I4/mmm$	0.3987		1.1111	0.08831
$CaFe_2As_2$	$Fmmm$	0.5432	0.5491	1.1388	0.08492
$Ca_{0.75}K_{0.25}Fe_2As_2$	$Pmmm$	0.5413	0.5473	1.1582	0.08579
$Ca_{0.5}K_{0.5}Fe_2As_2$	$Cmmm$	0.5397	0.5457	1.1660	0.08585
$Ca_{0.25}K_{0.75}Fe_2As_2$	$Pmmm$	0.5364	0.5423	1.2009	0.08734
KFe_2As_2	$Fmmm$	0.5345	0.5404	1.2122	0.08754

*f.u. stands for formula unit

Here, $a = b = 0.3987$ nm for the tetragonal structure ($I4/mmm$) of $CaFe_2As_2$ is 2.7% longer than the experimental value ($a = b = 0.3879$ nm), and $c = 1.1111$ nm is 5.3% shorter than the experimental value $c = 1.1740$ nm;[15] for the orthorhombic structure ($Fmmm$), $a = 0.5432$ nm, $b = 0.5491$ nm, and $c = 1.1388$ nm, are 0.3%, 0.27%, and 4.7% shorter than experimental values $a = 0.5450$ nm, $b = 0.5506$ nm, and $c = 1.1664$ nm[17] respectively. It can be found that the calculated length of the c axis and the volume of $Ca_{1-x}K_xFe_2As_2$ increase with the concentration of potassium ($x = 0$–1), but those of the a axis and the b axis decrease slightly with the content of potassium. This implies that the smaller number of valence electrons for K (only one) than that of Ca (two) would lead to a weaker bond with the FeAs layer.

3.2. Magnetic properties

Table 2 gives the values of total and local magnetic moments for $Ca_{1-x}K_xFe_2As_2$. It is obvious that the magnetism of $Ca_{1-x}K_xFe_2As_2$ comes mainly from Fe atoms, and increases with the potassium content. The calculated value of the Fe moment as $x = 0$ is 0.377 μ_B, smaller than the experimental value (0.8 μ_B) obtained by Goldman *et al.*[17]

Table 2. Total and local magnetic moments (μ_B/f.u.) of $Ca_{1-x}K_xFe_2As_2$.

x	0	0.25	0.5	0.75	1
Fe	0.377	0.558	0.669	0.764	0.822
total	0.682	1.009	1.211	1.382	1.487

Figure 2 gives the electronic bands of $CaFe_2As_2$ and KFe_2As_2. It can be found that the tops of occupied bands with the highest energy for both $CaFe_2As_2$ and KFe_2As_2 appear at Γ point, the profiles for $CaFe_2As_2$ are flatter than those for KFe_2As_2, and the band energy of spin-down for KFe_2As_2 is higher than that for $CaFe_2As_2$. The unoccupied bands with the lowest energy of $CaFe_2As_2$ are convex, and those of KFe_2As_2 are concave at the Γ point. The bottoms of all the unoccupied bands with the lowest energy appear at the X point. Almost all the spin-up band profiles of $CaFe_2As_2$ are similar to those of KFe_2As_2.

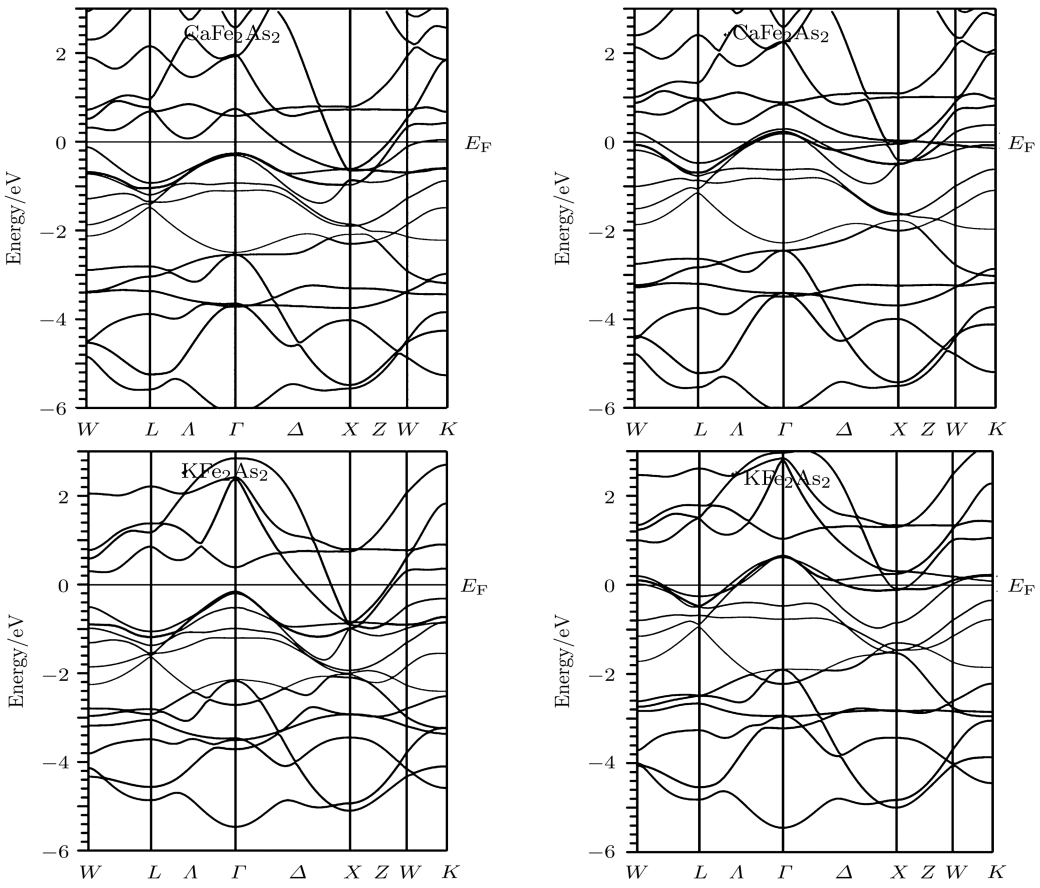


Fig. 2. Electronic band structures of CaFe2As2 and KFe_2As_2.

The spin-polarized densities of states (DOS) of $Ca_{1-x}K_xFe_2As_2$ are shown in Fig. 3. It is obvious that the DOS of Fe atoms is primary contributed to the total DOS of the compound. A DOS valley of spin-up and a right side of the primary spin-down peak of $CaFe_2As_2$ appear at the Fermi level. With the increase of K content, the energy of the primary DOS peak of spin-up below the Fermi level almost has no change, but its profile becomes higher and narrower. The energy of the primary peak spin-down DOS increases slightly with increasing K content, and the Fermi level moves from the right side to the top of the primary peak, which leads the magnetic moment of the system to increase.

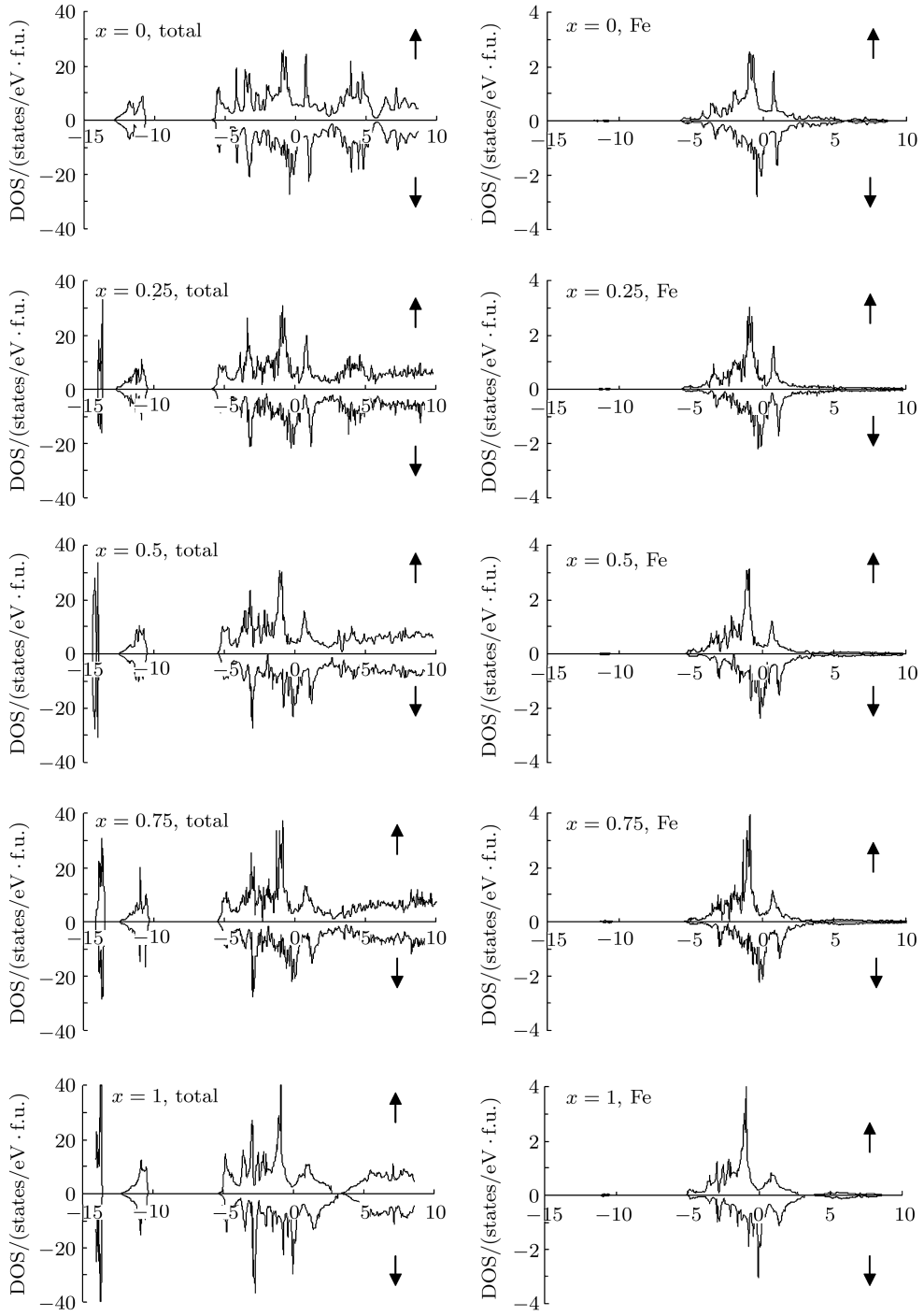


Fig. 3. Total and local spin-polarized densities of states $Ca_{1-x}K_xFe_2As_2$. The energy zero is the Fermi energy.

4. Conclusions

Based on density functional theory, using a full-potential linearized augmented plane wave and improved local orbital, the structures, the magnetism, the electronic bands, and the densities of states of the superconductivity $Ca_{1-x}K_xFe_2As_2$ compounds are optimized and calculated. The calculated magnetic moments of $Ca_{1-x}K_xFe_2As_2$ are analysed with the electronic bands and densities of states. The effects of K-doping on structure, magnetism, electronic bands, and densities of states are discussed. The calculation results indicate that with increasing K-doping the lengths of the a, b axes would decrease, but the length of the c axis, the volume, the energy of spin-down valence bands, and the DOS at the Fermi level would increase, which leads the magnetic moment of the system to increase.

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