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Electronic structure of AFe_2P_2, A = Ca,Sr,Ba[1]

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Abstract

The compounds $CaFe_2P_2$, $SrFe_2P_2$ and $BaFe_2P_2$ crystallize in the $ThCr_2Si_2$ structure which is a ternary variant of the $BaAl_4$ structure. In order to investigate the bonding properties, band-structure calculations using the full-potential linearized augmented plane wave (FLAPW) method have been performed. For the three compounds densities of states (DOS), local partial DOS and electron densities have been calculated. Compared to $CaNi_2P_2$ with a P–P distance of 2.30 Å, a value very close to that for a P–P single bond, this distance is 2.71 Å for $CaFe_2P_2$. While in the latter compound one still observes pronounced P–P(s–s and p–p) σ-bonds, this is not the case, apart from very weak p–p interactions, for $SrFe_2P_2$ and $BaFe_2P_2$ (P–P distances: 3.43 Å and 3.84 Å, respectively). Despite their different c/a ratios the Sr and Ba compounds show fairly similar bonding properties, in particular as far as the Fe–Fe and Fe–P interactions are concerned. In $BaFe_2P_2$, however, non-negligible interactions of the semicore [Ba(5p)] states with the P(3s) states are found. © 1997 Elsevier Science S.A.

Keywords: Electronic structure; Chemical bonding; Electron densities; Ternary phosphides; $ThCr_2Si_2$ structure

1. Introduction

The ternary phosphides $CaFe_2P_2$, $SrFe_2P_2$ and $BaFe_2P_2$ belong to the $ThCr_2Si_2$ structure (space group no. 139, I4/mmm) which was first described by Ban and Sikirica [1] for some silicides. More than 700 compounds with composition AB_2X_2 are known to crystallize in this structure where A can be an alkaline-earth or rare-earth element, B a transition metal atom (all the iron and platinum metals, but also, e.g. Cu, Zn and Mn) and X an element from groups 13–15 of the periodic table (mainly B, Al, Si, Ge, P, As and Sb). Many crystal structures of phosphides were determined among others by Mewis [2] and by Jeitschko et al. (e.g. [3] and references therein).

Many of these compounds show extraordinary physical properties, such as intermediate valency ($EuNi_2P_2$ [4,5]), superconductivity ($LaRu_2P_2$, $T_c = 4.1$ K [3]) as well as different magnetic structures [6] ranging from Pauli paramagnetism ($CaNi_2P_2$ [7]) to ferromagnetism ($LaCo_2P_2$ [5]) and antiferromagnetism with magnetic structures of sometimes great complexity ($EuCo_2P_2$ [8] where a non-collinear spin arrangement is observed).

According to Mewis [2], the alkaline-earth iron phosphides become increasingly graphite-like from the Ca to the Ba compound. This is in agreement with the structural situation. While in $SrFe_2P_2$ and $BaFe_2P_2$ the P–P distances are 3.43 Å and 3.84 Å, respectively, these two compounds can be assumed to be built up by $Fe_2P_2^{2-}$ layers with interspersed Sr^{2+} or Ba^{2+} ions. In $CaFe_2P_2$, however, the P–P distance is reduced to only 2.71 Å, a distance where already some bonding between the layers occurs. This also has consequences for the chemical properties. Whereas $CaFe_2P_2$ reacts slowly with dilute acids, a vigorous reaction is observed for the Sr and Ba compounds [2].

Theoretical investigations of the electronic structure for compounds crystallizing in the $ThCr_2Si_2$ structure are scarce. Several important papers refer to

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[1] Dedicated to Professor Herbert Boller on the occasion of his 60th birthday.

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calculations on the basis of the extended Hückel method [9–11]. The motivation for the first study of the electronic properties of $CaFe_2P_2$ and $CaNi_2P_2$ by means of the full-potential linearized augmented plane wave (FLAPW) method, performed recently by the present authors [12], was to investigate the influence of the transition metal on the bonding properties and in particular on the P–P distance. In this work, a comparison of the results for $SrFe_2P_2$ and $BaFe_2P_2$ with those for $CaFe_2P_2$, obtained by the same method, shall provide some insight into the changes caused when Ca is replaced by Sr or Ba.

2. Computational details

The electronic band-structures have been performed self-consistently by means of the linearized augmented plane-wave (LAPW) method [13,14] using the full-potential version (FLAPW method [15a, 15b]) with a Hedin–Lundqvist exchange-correlation potential [16]. The l expansion for the potential and the electron densities within the muffin-tin spheres was extended up to $l = 8$. Plane waves in the interstitial region were taken into account for the wave functions up to a length of $4(2\pi/a)$. For the self-consistency procedure 45 k- points in the irreducible part of the Brillouin zone (BZ) were used. The BZ integration was performed using the linearized tetrahedron method [17]. Because of the energetically high-lying Ba(5p) semicore states it was necessary to treat them as valence states in the band-structure calculation for $BaFe_2P_2$.

The unit cell for $CaFe_2P_2$, $SrFe_2P_2$ and $BaFe_2P_2$ is shown in Fig. 1 and the input parameters for the band-structure calculations are given in Table 1. The lattice parameters for the three compounds have been taken from Mewis [2]. In the following, for the designation of atomic orbitals, the z-axis is always chosen parallel to the c-axis of the unit cell.

3. Results

3.1. Densities of states

The DOS for $SrFe_2P_2$ and $BaFe_2P_2$ are shown in Fig. 2 whereas for $CaFe_2P_2$ the corresponding plot can be found in [12]. Apart from the peak caused by the Ba(5p) semicore states for the Ba compound, which exhibits a small but non-negligible P(s) contribution responsible for a weak covalent bonding interaction between these states, the lowest-lying valence states for all three compounds are those originating from the P(3s) states. The double-peak structure for $CaFe_2P_2$ is caused by the splitting of bonding and antibonding P–P(s–s) σ-states due to the relatively short P–P distance. The peaks above a gap of roughly 0.3 Ryd originate from overlapping P(3p) and Fe(3d) states, where the former dominate at lower energies and the latter at higher energies. This overlap indicates covalent bonding between P(p) and Fe(d) states as will be discussed later. For all three compounds the Fermi level (0.5574 Ryd for $CaFe_2P_2$, 0.49151 Ryd for $SrFe_2P_2$ and 0.56216 Ryd for $BaFe_2P_2$) lies below a peak that corresponds to antibonding Fe–Fe(d–d) interactions and that is occupied only in some compounds with $ThCr_2Si_2$ structure, e.g. in $CaNi_2P_2$ [12] where the Ni–Ni bonds are weaker than the Fe–Fe bonds in $CaFe_2P_2$.

Table 1
Input parameters for the band-structure calculations (in a.u.)

Quantity		$CaFe_2P_2$	$SrFe_2P_2$	$BaFe_2P_2$
Structural parameters	a	7.28489	7.22820	7.25655
	c	18.86891	21.94350	23.51197
	z_P	0.36430	0.35210	0.34560
Muffin-tin sphere radii	Ca/Sr/Ba	2.88000	3.00000	3.00000
	Fe	1.97892	1.97892	1.97892
	P	1.97892	1.97892	1.97892

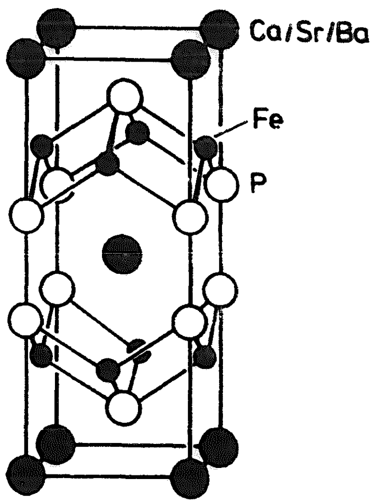

Fig. 1. Tetragonal unit cell for $CaFe_2P_2$, $SrFe_2P_2$ and $BaFe_2P_2$.

3.2. Electronic charges and ionicity

The total valence electron charges for the alkaline earth atomic spheres are reduced from 0.990 [12] for the Ca compound to 0.743 for the Sr compound although the muffin-tin sphere radius increases from 2.88 to 3.00 a.u. A similar but less pronounced trend is also found for the Fe spheres. This means a considerably higher ionicity, and thus chemical reactivity, for $SrFe_2P_2$ due to the larger P–P distance compared to $CaFe_2P_2$. For $BaFe_2P_2$ the valence electron charge in the Ba sphere is 0.999, but this high value compared to Sr is partly due to the different treatment of the semicore states in the two corresponding compounds, which influences the orthogonalization of the wave functions. Nevertheless, compared to the Sr

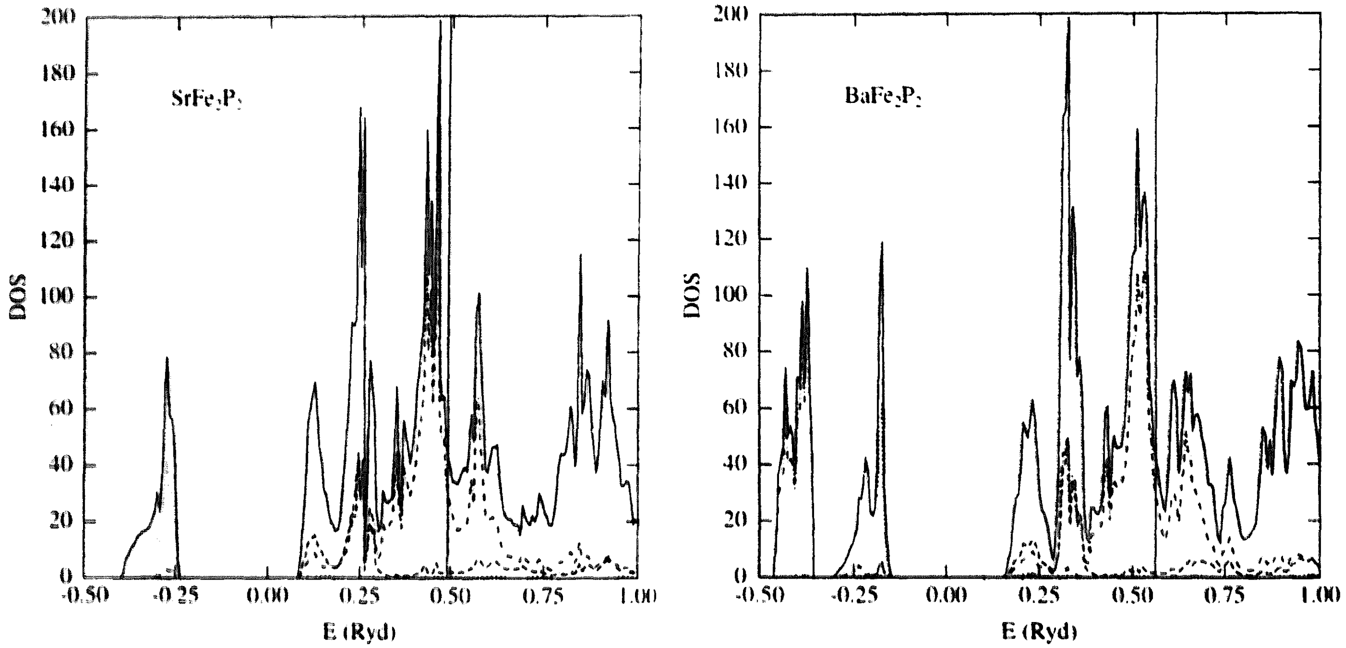

Fig. 2. Total DOS (——), P(s) (···), P(p) (- - -), Fe(d) (– · – ·) and Ba(5p) semicore (– · · –) local partial DOS components for $SrFe_2P_2$ (left) and $BaFe_2P_2$ (right) in units of one-electron states per Rydberg and per unit cell. The Fermi energy is indicated by a vertical line.

compound, the ionicity of Ba in $BaFe_2P_2$ seems to be reduced. As shown below, this is accompanied by stronger covalent Ba–Ba bonds (even though the interaction between the Sr and Ba atoms, respectively, has a pronounced ionic and thus repulsive component). However, the electronic charge in the Fe sphere of $BaFe_2P_2$ is even smaller than for $SrFe_2P_2$ suggesting a further increase of the ionicity of Fe in this compound.

3.3. Electron densities and chemical bonding

The valence electron densities for $SrFe_2P_2$ and $BaFe_2P_2$ are presented in Figs. 3 and 4. The corresponding information for $CaFe_2P_2$ can be found in Figs. 11 and 12 of Gustenau et al. [12]. From the plots for the (100) plane it can be seen that the density within the $Fe_2P_2^{2-}$ layers is almost independent of the interlayer distance. The plots for the (001) planes show a nearly identical valence electron density for the plane through the Fe atoms, while in the plane through the Sr/Ba atoms the minimum density between these atoms is 0.031 e Å^{-3} for $SrFe_2P_2$ and 0.045 e Å^{-3} for $BaFe_2P_2$ indicating stronger covalent bonds for the Ba compound. (The value of 0.052 e Å^{-3} in $CaFe_2P_2$ does not indicate an even stronger bond between the Ca atoms, but is caused by a contribution of the relatively strong P–P bond perpendicular to this plane.)

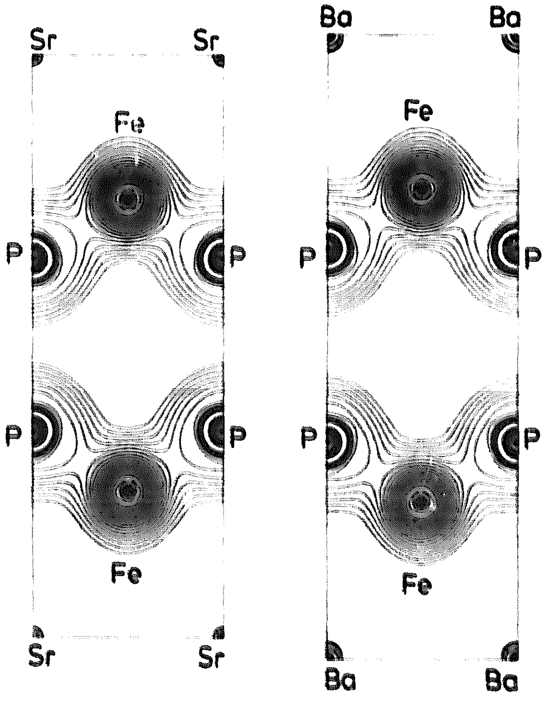

Fig. 3. Valence electron densities in the (100) plane for $SrFe_2P_2$ (left) and $BaFe_2P_2$ (right). A logarithmic grid of contour lines has been used ($x_i = x_0\,2^{i/2}$, $x_0 = 0.2$ e Å^{-3}).

The fact that the P–P distances are as long as 3.43 Å for $SrFe_2P_2$ and 3.84 Å for $BaFe_2P_2$ does not mean that there are no bonding P–P interactions. The electron densities in the (100) plane for states with Γ symmetry (Fig. 5, Table 2) demonstrate the existence of weak P–P(p_z–p_z) bonds [the P(p_z) states are also involved in interactions with Fe(d_{z^2}) states]. A similar

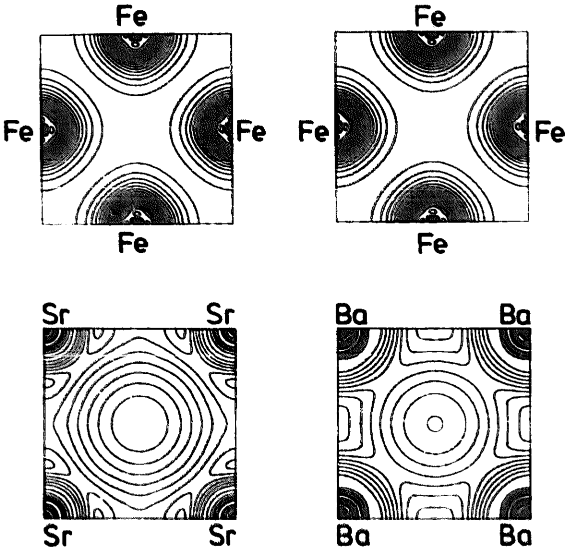

Fig. 4. Valence electron densities in the (001) planes through the Fe atoms (top row) and through the Sr or Ba atoms (bottom row) for $SrFe_2P_2$ (left) and $BaFe_2P_2$ (right). A logarithmic grid of contour lines has been used ($x_i = x_0\ 2^{i/3}$, $x_0 = 0.02$ e Å^{-3}).

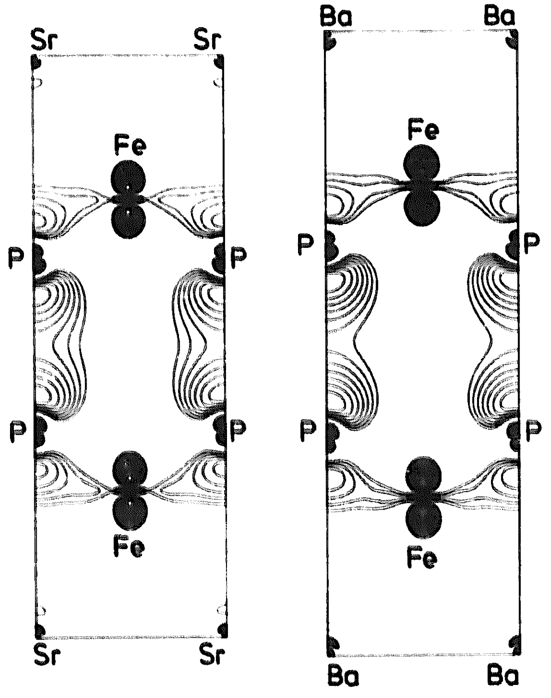

Fig. 5. Electron densities in the (100) plane for the Γ-state at 0.0861 Ryd for $SrFe_2P_2$ (left) and at 0.1925 Ryd for $BaFe_2P_2$ (right). A logarithmic grid of contour lines has been used ($x_i = x_0\ 2^{i/3}$, $x_0 = 0.02$ e Å^{-3}). For a charge analysis of these states see Table 2.

Table 2
Partial changes (in percent) for the two states for which electron density plots are presented in this paper

		$SrFe_2P_2$				$BaFe_2P_2$			
k	*l*	*E* (Ryd)	Sr	Fe	P	*E* (Ryd)	Ba	Fe	P
Γ	s	0.0861	4.8	4.1	1.1	0.1925	3.8	3.6	2.1
	p		0.0	0.0	21.6		0.0	0.0	20.8
	d		2.4	11.4	0.0		1.7	12.8	0.0
Z	s	0.4670	0.7	0.0	1.7	0.5161	1.5	0.0	1.2
	p		0.0	3.9	5.4		0.0	3.1	3.8
	d		18.5	11.9	3.3		18.7	9.3	2.7

Note: The energies are given with respect to the average potential in the interstitial region.

plot for $CaFe_2P_2$ (Fig. 5 of Gustenau et al. [12]) is characteristic for the much stronger P–P bond in the Ca compound.

Finally, a type of bond not present in $CaFe_2P_2$ (because the corresponding states are unoccupied) is shown in Fig. 6. It is caused by the overlap of P(p_z) orbitals with the toroidal lobe of the Sr/Ba(d_{z^2}) orbital.

4. Conclusions

The replacement of Ca in $CaFe_2P_2$ by Sr and Ba leads to a considerably increased distance between the $Fe_2P_2^{2-}$ layers and therefore to enhanced P–P distances. The P–P bonds, already weak in the Ca compound, become even weaker for $SrFe_2P_2$ and $BaFe_2P_2$ which is accompanied by a higher ionicity of these compounds and by a weakening of the covalent bonds except for (i) the Sr/Ba–P(d_{z^2}–p_z) interactions not present in $CaFe_2P_2$ where the corresponding

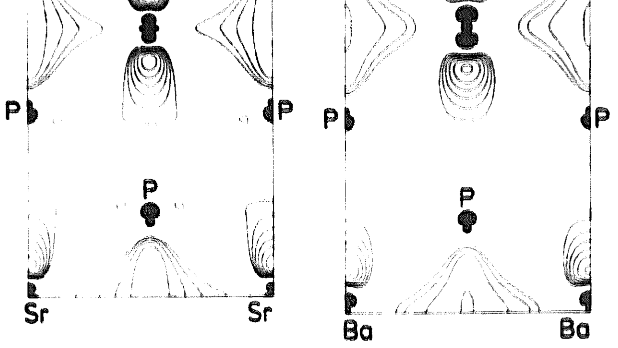

Fig. 6. Electron densities in the (110) plane for the *Z*-state at 0.4670 Ryd for $SrFe_2P_2$ (left) and at 0.5161 Ryd for $BaFe_2P_2$ (right). A logarithmic grid of contour lines has been used ($x_i = x_0\ 2^{i/3}$, $x_0 = 0.02$ e Å^{-3}). For a change analysis of these states see Table 2.

states lie above the Fermi level, (ii) the covalent bonds between the alkaline earth atoms in the (001) plane due to more pronounced overlap of the wave functions with increasing principal quantum number and (iii) the non-negligible interaction between the Ba(5p) semicore and P(3s) valence states in $BaFe_2P_2$.

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References

[1] Z. Ban, M. Sikirica, Acta. Crystallogr. 18 (1965) 594.
[2] A. Mewis, Z. Naturforsch. 35b (1980) 141.
[3] W. Jeitschko, R. Glaum, L. Boonk, J. Solid State Chem. 69 (1987) 93.
[4] E.V. Sampathkumaran, G. Wortmann, G. Kaindl, J. Magn. Magn. Mater. 54/57 (1986) 347.
[5] E. Mörsen, B.D. Mosel, W. Müller-Warmuth, M. Reehuis, W. Jeitschko, J. Phys. Chem. Solids 49 (1988) 785.
[6] A. Szytula, J. Leciejewicz, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earth, vol. 12, Elsevier, Amsterdam, 1989, p. 133.
[7] W. Jeitschko, M. Reehuis, J. Phys. Chem. Solids 48 (1987) 667.
[8] M. Reehuis, W. Jeitschko, M.H. Möller, P.J. Brown, J. Phys. Chem. Solids 53 (1992) 687.
[9] R. Hoffmann, C. Zheng, J. Phys. Chem. 89 (1985) 4175.
[10] C. Zheng, R. Hoffmann, J. Solid State Chem. 72 (1988) 58.
[11] C. Zheng, J. Am. Chem. Soc. 115 (1993) 1047.
[12] E. Gustenau, P. Herzig, A. Neckel, J. Solid State Chem. 129 (1997) 147.
[13] O.K. Anderson, Phys. Rev. B. 12 (1975) 3060.
[14] D.D. Koelling, G.O. Arbmann, J. Phys. F: Met. Phys. 5 (1975) 2041.
[15a] E. Wimmer, H. Krakauer, M. Weinert, A.J. Freeman, Phys. Rev. B 24 (1981) 864.
[15b] H.F.J. Hansen, A.J. Freeman, Phys. Rev. B 30 (1984) 561.
[16] L. Hedin, S. Lundqvist, J. Phys. (Paris) 33 (1972) C3-73.
[17] G. Lehmann, M. Taut, Phys. Status Solidi B 54 (1972) 469.