

BONDING AND STABILITY IN THE ORDERED ALLOYS FeV AND CoTi. COMPARISON WITH FeTi

Štěpán PICK^a, Mojmir TOMÁŠEK^a and Mojmir ŠOB^b

^a *J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2 and*

^b *Institute of Physical Metallurgy, Czechoslovak Academy of Sciences, 616 62 Brno*

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Partial wave analysis together with the qualitative examination of hybridization has been performed for two ordered intermetallic alloys with CsCl structure, FeV, and CoTi. The results resemble those obtained previously for FeTi, although important deviations are present as well. The stabilization of the ordered phase is again due to ionic effects. Qualitative arguments are suggested to explain the small stability of the CsCl phase of FeV and some differences in the FeTi and CoTi phase diagrams.

There is a growing interest in the understanding of the electronic properties of metallic alloys important in technological applications. Recently, the present authors studied¹ two representatives of the family of ordered intermetallic alloys with CsCl structure, namely, FeTi and FeAl. The computed energy band structure² of these alloys together with the so-called qualitative theory of Shockley surface states^{1,3,4} served as main tools of the analysis. Since then, detailed information on the electronic energy bands of two related alloys, FeV and CoTi, became available⁵. These materials differ only "slightly" from FeTi studied previously¹ (they have by one electron more in the elementary cell). It is the aim of the present paper to check whether main conclusions of ref.¹ remain unchanged for FeV and CoTi as well.

THEORETICAL

The APW electronic energy band structure calculation⁵ with the Slater exchange contribution included was employed as described elsewhere². Although the calculation is not self-consistent, previous applications of the same procedure have shown^{2,6} its reliability upon the condition of a proper choice of the electronic configuration of the metal atoms. As far as the electronic properties of FeV and CoTi are concerned, only a very limited amount of information has been published until now. FeV has been studied only experimentally⁷, whereas for CoTi certain theoretical results exist^{8,9} together with XPS experiments¹⁰.

The method of the analysis of the energy band structure is the same as in ref.¹ (see also ref.⁴) and hence, it will not be explained here.

RESULTS AND DISCUSSION

Table I summarizes the sizes of muffin-tin spheres used in the APW calculation⁵ and shows which part of the elementary cell is occupied by them. Generally, the muffin-tin sphere radii reflect the well known chemical trend¹¹, where the (say, metallic) atomic radii decrease from left to right in the Periodic Table (of course, the definition of metallic radii is more problematic for transition metals¹¹ and, besides that, a slight ionicity is present in a varying degree for the alloys considered). The A–B bond contraction is also given, the magnitude of which can indicate the degree of the stabilization of the CsCl phase^{11–13}.

It is quite interesting that phase diagrams of FeTi and CoTi are rather similar^{14,15}. However, the CsCl phase of FeTi is more sensitive to the deviations from the stoichiometry than the CoTi one. The CsCl phase of FeV was found^{12,13} to exist as a metastable phase for temperatures below about 870 K.

In Tables II–VII, the energies of several energy branches of FeV for selected Brillouin zone points are presented together with the respective partial wave analysis. For comparison, the energy values for CoTi are given in the parentheses. These energy branches delimit the gaps, which are either hybridizational (HG) or non-hybridizational^{1,3,4} (NHG). Tables II–VII correspond to Tables I–VI of ref.¹ for FeTi.

Direct comparison shows that the results for FeTi and FeV are similar. Moreover, it is seen that for FeV, as confronted with the behaviour of the Ti component in FeTi, there is a larger amount of states of V character in the lower (occupied) levels. This behaviour reflects the existence of an extra electron of V as compared with Ti. When

TABLE I

Several data characterizing the geometry of intermetallic alloys with CsCl structure (AB = FeTi, FeV, CoTi) are summarized. a is the lattice constant (a.u.) and δ_{AB} is the A–B bond contraction (a.u.) as compared with the metallic radii sum prediction^{12,13}, r_A , r_B are the muffin-tin sphere radii (a.u.) and V_A , V_B (%) are the corresponding muffin-tin sphere volumes within the elementary cell. V_{out} (%) characterizes the "out of sphere" region. 1 a.u. = $0.529 \cdot 10^{-8}$ m

Alloy AB	a	r_A	r_B	δ_{AB}	V_A	V_B	V_{out}
FeTi	5.6241	2.3965	2.4741	0.157	32.408	35.661	31.931
FeV	5.4992	2.3496	2.4128	0.095	32.674	35.380	31.946
CoTi	5.6525	2.3954	2.4998	0.119	31.878	36.233	31.889

going from FeV to CoTi, the Co component in the lower levels of CoTi is larger typically by about 7–15% than the corresponding Fe component of FeV. This is

TABLE II

Partial wave analysis for two energy branches delimiting the NHG in Δ_2 states of FeV. Irreducible representations (IR), energy from ref.⁵, and partial charges inside the muffin-tin spheres (Fe or V) are shown. The "missing" charge (to 100%) falls essentially outside the muffin-tin spheres. In parentheses, the corresponding energy values for CoTi are also presented. $E_F = 0.755$ Ry for FeV and 0.69 Ry for CoTi. $1 \text{ Ry} = 2.178 \cdot 10^{-18} \text{ J}$

Point:	Γ	Δ (middle)	X
IR	12	2	3'
$E(\text{Ry})$	0.8178 (0.7651)	0.7697 (0.7351)	0.6949 (0.6951)
$C(\text{Fe})\%$	$35.738e_g$	$26.785e_g$	0
$C(\text{V})\%$	$58.079e_g$	$62.679e_g$	$82.032e_g$
IR	12	2	2
$E(\text{Ry})$	0.4442 (0.3842)	0.4849 (0.4129)	0.5492 (0.4488)
$C(\text{Fe})\%$	$56.943e_g$	$63.307e_g$	$87.569e_g$
$C(\text{V})\%$	$24.635e_g$	$19.697e_g$	0

TABLE III

Partial wave analysis for two energy branches delimiting the NHG in Δ_2 states of FeV

Point:	Γ	Δ (middle)	X
IR	25'	2'	2'
$E(\text{Ry})$	0.9559 (0.9532)	0.9362 (0.9425)	0.9137 (0.9312)
$C(\text{Fe})\%$	$13.795t_{2g}$	$8.189t_{2g}$	0
$C(\text{V})\%$	$84.194t_{2g}$	$88.802t_{2g}$	$95.884t_{2g}$
IR	25'	2'	3
$E(\text{Ry})$	0.6343 (0.5255)	0.6594 (0.5338)	0.6779 (0.5426)
$C(\text{Fe})\%$	$84.647t_{2g}$	$89.569t_{2g}$	$97.085t_{2g}$
$C(\text{V})\%$	$12.275t_{2g}$	$7.372t_{2g}$	0

TABLE IV
 Partial wave analysis for two energy branches delimiting the NHG in Δ_5 states of FeV

Point:	Γ	Δ (middle)	X
IR	25'	5	5'
$E(\text{Ry})$	0.9559 (0.9532)	0.8732 (0.8673)	0.8085 (0.8057)
$C(\text{Fe})\%$	13.795 t_{2g}	7.035 t_{2g} 3.645 p	4.970 p
$C(\text{V})\%$	84.194 t_{2g}	81.121 t_{2g} 0.850 p	85.617 t_{2g}
IR	25'	5	5
$E(\text{Ry})$	0.6343 (0.5255)	0.6372 (0.5189)	0.6311 (0.5112)
$C(\text{Fe})\%$	84.647 t_{2g}	87.404 t_{2g} 0.015 p	92.562 t_{2g}
$C(\text{V})\%$	12.275 t_{2g}	7.356 t_{2g} 0.886 p	2.093 p

TABLE V
 Partial wave analysis for two energy branches delimiting the NHG in Σ_3 states of FeV

Point:	Γ	Σ (middle)	M
IR	25'	3	5
$E(\text{Ry})$	0.9559 (0.9532)	0.8656 (0.8654)	0.9529 (0.9209)
$C(\text{Fe})\%$	13.795 t_{2g}	4.099 t_{2g} 2.808 p	26.944 t_{2g}
$C(\text{V})\%$	84.194 t_{2g}	86.635 t_{2g} 0.083 p	71.092 t_{2g}
IR	25'	3	5
$E(\text{Ry})$	0.6343 (0.5255)	0.6482 (0.5246)	0.5651 (0.4743)
$C(\text{Fe})\%$	84.647 t_{2g}	90.859 t_{2g} 0.279 p	71.404 t_{2g}
$C(\text{V})\%$	12.275 t_{2g}	2.745 t_{2g} 1.246 p	21.809 t_{2g}

again explained by the change of the number of electrons on the respective atoms. Besides that, the mutual positions of (X_1 (upper), X_3) and (R_{12} , R_{15}) pairs of energy levels are interchanged for CoTi as compared with FeV (and FeTi).

The gaps delimited by energy branches considered are of the same character for FeTi, FeV, and CoTi. The only exception occurs for CoTi (see Table VII and also Table VI of ref.¹) – due to the above mentioned change of energy levels in point R, the second HG in A_3 states is transformed into a narrow NHG of the width $E(R_{15}) - E(R_{12}) = 0.025$ Ry.

TABLE VI

Partial wave analysis for three energy branches delimiting two HG in A_1 states of FeV

Point:	Γ	A (middle)	R
IR	25'	1	1
$E(\text{Ry})$	0.9559 (0.9532)	0.9070 (0.8705)	1.4260 (1.2094)
C(Fe)%	13.795 t_{2g}	22.231 t_{2g} 4.000 p 0.017 s	74.078 s
C(V)%	84.194 t_{2g}	60.862 t_{2g} 1.551 p 3.195 s	0
IR	25'	1	15
$E(\text{Ry})$	0.6343 (0.5255)	0.5855 (0.4902)	0.6057 (0.5706)
C(Fe)%	84.647 t_{2g}	67.392 t_{2g} 0.007 p 3.534 s	16.678 t_{2g}
C(V)%	12.275 t_{2g}	17.846 t_{2g} 0.585 p 1.220 s	61.179 t_{2g}
IR	1	1	25'
$E(\text{Ry})$	0.1755 (0.1427)	0.4089 (0.3633)	0.5476 (0.4585)
C(Fe)%	32.792 s	5.231 t_{2g} 7.784 p 21.856 s	80.238 t_{2g}
C(V)%	27.692 s	4.265 t_{2g} 8.033 p 15.886 s	8.312 p

The position of the Fermi energy E_F with respect to the energy bands deserves an analysis ($E_F = 0.755$ Ry for FeV, 0.69 Ry for CoTi (ref.⁵), and 0.69 Ry for FeTi (ref.^{1,2}), all values refer to the muffin-tin zero). A closer examination reveals

TABLE VII
Partial wave analysis for four energy branches delimiting three HG in A_3 states of FeV

Point:	Γ	A (middle)	R
IR	25'	3	12'
$E(\text{Ry})$	0.9559 (0.9532)	0.8767 (0.8561)	0.9733 (0.9959)
$C(\text{Fe})\%$	13.795 t_{2g}	18.201 d^a 1.508 p	0
$C(\text{V})\%$	84.194 t_{2g}	73.675 d 0.017 p	98.342 e_g
IR	12	3	12
$E(\text{Ry})$	0.8178 (0.7651)	0.8161 (0.7585)	0.7127 (0.5681)
$C(\text{Fe})\%$	35.738 e_g	34.148 d 3.704 p	98.709 e_g
$C(\text{V})\%$	58.079 e_g	52.588 d 1.868 p	0
IR	25'	3	15
$E(\text{Ry})$	0.6343 (0.5255)	0.5855 (0.4878)	0.6057 (0.5706)
$C(\text{Fe})\%$	84.647 t_{2g}	74.560 d 0.408 p	16.678 p
$C(\text{V})\%$	12.275 t_{2g}	15.735 d 1.319 p	61.179 t_{2g}
IR	12	3	25'
$E(\text{Ry})$	0.4442 (0.3842)	0.5425 (0.4606)	0.5476 (0.4585)
$C(\text{Fe})\%$	56.943 e_g	59.132 d 4.441 p	80.238 t_{2g}
$C(\text{V})\%$	24.635 e_g	15.218 d 3.586 p	8.312 p

^a $d = e_g + t_{2g}$.

that E_F for CoTi, as compared with FeTi, is slightly shifted upwards with respect to the bands. On the other hand, when compared with FeTi and CoTi, both the occupied and empty bands for FeV move towards E_F and the gaps become narrower.

One finds many similarities in the electronic structure of FeTi, CoTi, and FeV near E_F . This indicates that the ionicity (bond polarization¹¹) is the main stabilizing mechanism^{1,12}. In some respect, the difference between FeTi and CoTi seems to be quantitative rather than qualitative. It should not be overlooked, however, that the Fermi surface has predominantly negative (hole) character in CoTi and positive (electronic) character in FeTi (ref.⁸). Although the situation here is much more complicated than *e.g.* for CuZn (ref.¹⁶), one can expect that the Fermi surface changes (especially near the Brillouin zone boundary) invoked by deviations from the stoichiometry play a great role in the stability of the CsCl phase. Namely, when Ti concentration decreases (*i.e.* the electron density grows), the Fermi surface should expand for FeTi and shrink for CoTi. Hence, one is tempted to guess that the response of FeTi to the change of Ti concentration is opposite to that of CoTi, namely, the region of the CsCl phase existence extends more towards the Co-rich phases for CoTi and towards the Ti-rich alloy for FeTi, in agreement with experiment^{14,15}.

For FeV, the Fe and V derived bands move closer to E_F . This effect can be explained as the result of the smaller difference of Fe and V electronegativities¹¹ (as compared with Co and Ti). Hence, a smaller ionicity as well as stability may be predicted. Besides that, appearance of more electronic states near E_F is well known to work often against the stability of the given structure (*via e.g.* the Jahn–Teller or pseudo-Jahn–Teller effects, Peierls transition, Stoner criterion of ferromagnetism *etc.*).

In conclusion, let us discuss the possible existence of surface states. Similarly as for FeTi (ref.¹), there are important HG in A_1 and A_3 states of FeV (Tables VI, VII), where Shockley surface states can appear. As mentioned above, the most important (central) HG in A_3 states disappears for CoTi. As discussed recently¹⁷ in detail, the so-called heteroatomic surface states¹⁸ are formed easily^{18,19} (*cf.* also the results of ref.²⁰) in NHG of AB-type alloys or compounds supposing that the hybridization between A and B states is still considerable. However, this is not the present case. Indeed, the energy branches delimiting the corresponding NHG have always strong A or B character, thus differing from the situation described in ref.¹⁷. Only Tamm surface states^{17,18} can appear in these gaps supposing that the self-consistency effects and the Madelung potential changes²¹ at the surface exceed the quantity $W/2$ (W is the width of an energy band from which the surface state can originate). As noted in a different context²⁰, such an effect should be accompanied by a surface core-level shift detectable experimentally. If it actually takes place, this effect is expected to be more pronounced for polar surfaces containing one type of atoms only^{21,22}, *e.g.* for (001) and (111) surfaces of CsCl crystals.

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