(PS6)

Internal parameter dependence of electronic band structure for $CoAs_3$

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The filled skutterudite RT_4X_{12} (R= rare earth; T = Fe, Ru and Os; X = P, As and Sb) crystallizes in a unique BCC structure of a space group $Im\bar{3}$ (T_h^5, # 204). The atom positions are the following: R in 2a: (0, 0, 0), T in 8c: (1/4, 1/4, 1/4) and X in 24g: (0, u, v). The six X atoms form an octahedral environment for the T atom and the twelve X atoms an icosahedral environment for the R atom.[1]

In order to investigate the internal parameters u and v dependence of the electronic band structure, the binary skutterudite $T'X_3$ (T' = Co, Rh, Ir) is suitable because the R sites are empty. We have calculated the band structure of $CoAs_3$ for three hypothetic cases and one real case. The lattice constant ($a = 8.195$ Å) and the nearest neighbor distance (2.334 Å) between Co and As atoms are fixed as those of observed values.[2]

A) Ideal octahedral case, $u - 2uv = 3/8 - v$. ($u = 0.3275$ and $v = 0.1377$.)
B) Experimentally observed values, $u = 0.3431$ and $v = 0.1503$.[2]
C) Oftedal's relation case, $u + v = 1/2$. The short edge of icosahedron $2v$ is equal to the first nearest neighbor distance of inter-icosahedron $(1 - 2u)$. ($u = 0.3465$ and $v = 0.1535$.)
D) Symmetrical case of A about the Oftedal's line, $u = 1/2 - v_A$ and $v = 1/2 - u_A$. ($u = 0.3623$ and $v = 0.1725$.)

We show the resultant band structures in the vicinity of the Fermi level E_F in Fig.1.

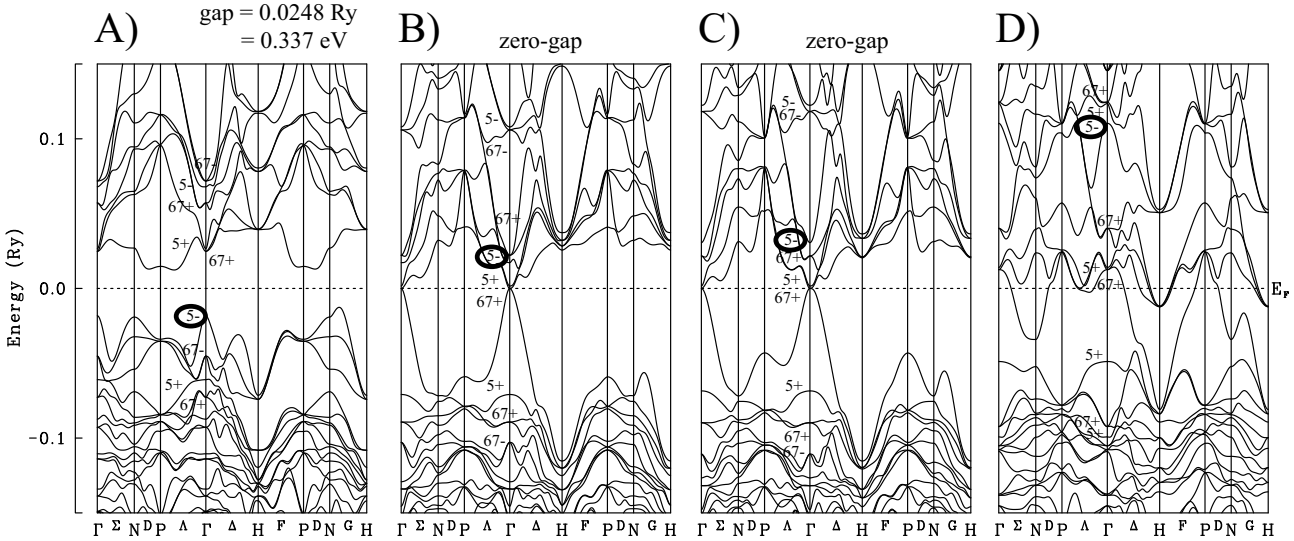

Figure 1: The FLAPW band structures of $CoAs_3$ for cases A∼D.

In Figure 1, the Γ_5^- state marked by oval consists mainly of the a_u molecular orbital from the As p states at each corner of the As_{12} icosahedron.[3] As decreasing the inter-icosahedron distance (from case A to D), the energy of Γ_5^- state increases gradually due to increase of the two-center integral for the As_{12} p molecular orbitales.

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[3] H. Harima and K. Takegahara: J. Phys.: Condens. Matter **15** (2003) S2081.