Crystal structures of $Co_{1-x}Fe_xTiSb$ compounds

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Half-Heusler compounds with unusual electronic properties

CoTiSb belongs to the family of half-Heusler compounds [1] which have the general form XYZ, with X and Y transition metals and Z an sp electron metal.

These materials are thought to have the MaAgAs type structure, derived from the general Heusler structure (X2Y Z) by leaving every other X site vacant.

The latter is thought to lead to unusual electronic properties, including the so-called half-metallic ferromagnetism with a 100% polarized electronic band responsible for the metallic conduction [2].

In addition, the ferromagnetism in this series has been claimed to be associated with a metal to semiconductor transition [3].

All this makes the half metallic ferromagnets of this family good candidates for potential applications involving spin-polarized transport (spintronics) [4].

The $Co_xFe_{1-x}TiSb$ samples for this investigation (x = 0, x = 0.015 and x = 0.05) have very different transport properties what is shown in Figure 1.

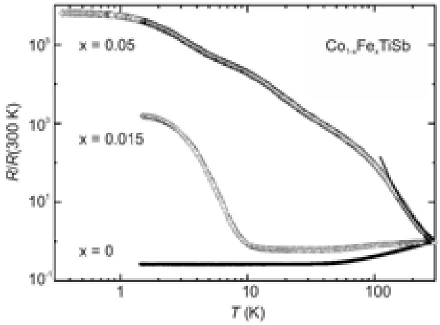

***Figure 1**: Normalized dc-resistances R(T)/R(300 K)[3]*

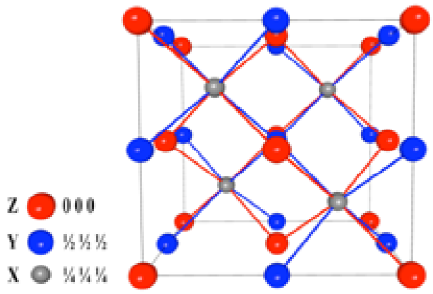

***Figure 2**: Representation of the structure of Half Heusler compounds, F-4 3 m. X, Y and Z represent the coordinates of Co, Ti and Sb, respectively, in the ideal structure.*

According to electronic band structure calculations [4], should be a paramagnetic semiconductor with an energy gap of the order of 1 eV. However, the situation is complicated because the results are very sensitive to which elements occupy the X, Y and Z positions (Fig. 2) in the structure [5].

For instance, CoTiSb ought to be a nonmagnetic semimetal, and TiCoSb a ferromagnetic metal. Although this claim obtained some support from measurements on a polycrystalline sample of CoTiSb, it was seriously questioned by recent work on single crystals of CoTiSb [6,7]. In fact none of the above possibilities matched the experimental results.

In addition it was found that replacing a small amount (5 %) of Co by Fe strongly reduces the low temperature electrical conductivity, by nearly 2 orders of magnitude.

This clearly shows that the sample is close to a metal-semiconductor instability.
In addition the properties of CoTiSb are sensitive to details of the annealing of the sample.

SHELXL refinement from BM1A SNBL ESRF CCD X-ray data (T = 100 K)

$Co_{1-x}Fe_xTiSb$; x = 0; λ = 0.7173	
Space group; Z	F-43m; 4
a (Å)	5.8919 (5)
Reflections measured	3123
Reflections used	108
R_{int} ; S	0.0386; 1.191
R; R_w	0.0175; 0.0460
Largest Δρ (x,y,z) max; min (e/Å³)	1.003 ; -1.619
Extinction coefficient	0.0068(3)
Flack parameter	0.2(2)
Co (¹/₄,¹/₄,¹/₄) Uiso	0.00558(7)
Ti (¹/₂,¹/₂,¹/₂) Uiso	0.00570(8)
Sb (0,0,0) Uiso	0.00635(3)

All refinements: No constraints/restraints
No correlation matrix elements larger than 0.500

$Co_{1-x}Fe_xTiSb$; x = 0.015; λ = 0.7173	
Space group; Z	F-43m; 4
a (Å)	5.8933 (6)
Reflections measured	3638
Reflections used	117
R_{int} ; S	0.0429; 1.179
R; R_w	0.0240; 0.0560
Largest Δρ (x,y,z) max; min (e/Å³)	2.828; -2.162
Extinction coefficient	0.1323(18)
Flack parameter	0.25(19)
Co (¹/₄,¹/₄,¹/₄) Uiso	0.00508(8)
Co Occupancy	0.983(4)
Fe (¹/₄,¹/₄,¹/₄) Uiso	0.005 FIX
Fe Occupancy	0.019(4)
Ti (¹/₂,¹/₂,¹/₂) Uiso	0.00533(8)
Sb (0,0,0) Uiso	0.00486(3)

$Co_{1-x}Fe_xTiSb$; x = 0.05; λ = 0.721839	
Space group; Z	F-43m; 4
a (Å)	5.8946 (7)
Reflections measured	5912
Reflections used	101
R_{int} ; S	0.0572; 1.119
R; R_w	0.0138; 0.0342
Largest Δρ (x,y,z) max; min (e/Å³)	0.671; -1.473
Extinction coefficient	0.1171(9)
Flack parameter	0.21(16)
Co (¹/₄,¹/₄,¹/₄) Uiso	0.00555(8)
Co Occupancy	0.952(3)
Fe (¹/₄,¹/₄,¹/₄) Uiso	0.0056(15)
Fe Occupancy	0.055(3)
Ti (¹/₂,¹/₂,¹/₂) Uiso	0.00584(7)
Sb (0,0,0) Uiso	0.00417(2)

JANA 2006 joint Neutron TriCS PSI / X-ray data SNBL refinement; x = 0.05

For all three samples (x = 0, x = 0.015 and x = 0.05) neutron single crystal measurements on TriCS (PSI) and X-ray single crystal measurements on BM1A beamline (SNBL/ESRF) each at 100 K has been carried out. It is planned to carry out joint refinement (neutron- and the X-ray) on all three samples

Presented in the table on the right are preliminary refinement results on the joint refinement on the neutron- and the X-ray datasets with x = 0.05, with a new beta-version of the JANA2006 software [8].

	X-ray (SNBL)	Neutron (TriCS)
λ (Å)	0.721839	1.1807
Extinction giso	0.206374	0.003752
Reflections	1263	447 + 15
GOF (obs) single	0.0171	0.0171
GOF (obs) joint	0.0171	
R (obs) single	0.0355	0.0276
R (obs) joint	0.0351	
R_w (obs) single	0.0434	0.0319
R_w (obs) joint	0.0345	
Maximum change/s.u.	for giso (Neutron) 0.0268	
Largest Δρ (x,y,z) max; min	0.276 e/Å³ ; -0.306 e/Å³	

Refinement conditions:
Restric: Occupancy Co + Fe = 1
Equation : Uiso[Fe] = Uiso[Co]

Correlations:
0.98 correlation for:
scale[Neutrons]/giso[Neutrons]

Co (¹/₄,¹/₄,¹/₄) Uiso	-0.0047(2)
Co Occupancy	0.944(3)
Fe (¹/₄,¹/₄,¹/₄) Uiso	-0.0047
Fe Occupancy	0.0557
Ti (¹/₂,¹/₂,¹/₂) Uiso	-0.0052(3)
Sb (0,0,0) Uiso	-0.0047(2)

Reference: (1) M. Terada, K. Endo, Y. Fujita, and R. Kumura, J. Phys. Soc. Jpn. 32, 91 (1972); (2) R. A. De Groot, F. M. Muller, P.G. Van Engen, and K.H. Buschow, Phys. Rev. Lett., 50, 2024 (1983); (3) M.A. Kouacou, J. Pierre, and R.V. Skolozdra, J. Phys.: Condens. Matter 7, 7373 (1995); (4) B.R.K. Nanda and I. Dasgupta, J. Phys. Condens. Matter 17, 5037 (2005); (5) S. Ishida, T. Masaki, S. Fujii, and S. Asano, Physica B Vol. 239, 163 (1997); (6) L. Degiorgi, A. V. Sologubenko, H. R. Ott, F. Drymiotis and Z. Fisk, Phys. Rev. B, 65, 41101 (2001); (7) H.R. Ott, Physica B, 318, 77 (2002); (8) V. Petricek et al., JANA, Inst. of Physics, AVCR, Praha, Czech. Rep. (2000).

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