Electronic Structure Calculations for Cr$_{1-x}$Al$_x$

CNF Project # 1845-09  
Principal Investigator(s): Frances Hellman  
User(s): Zoe Boekelheide

Affiliation(s): Materials Science Department, Lawrence Berkeley National Lab and Physics Department, University of California-Berkeley  
Primary Research Funding: Department of Energy  
Contact: fhellman@berkeley.edu, zboekelheide@berkeley.edu

Abstract:

Cr$_{1-x}$Al$_x$ is antiferromagnetic and exhibits semiconductor behavior for $x = 15-26$ at. percent, which until now has not been explained by theory. Electronic structure calculations for disordered Cr$_{0.80}$Al$_{0.20}$ show a partial gap at the Fermi energy and compare well to photoemission measurements of the valence band of a thin film samples.

Summary of Research:

Intermetallic compounds containing transition metals and $sp$ elements often form a gap at the Fermi energy due to hybridization. This gap can be exploited for applications, making these compounds the subject of intense study. For example, intermetallic semiconductors are attractive for use in thermoelectric devices due to their typically small gaps and large Seebeck coefficients (ex. ZrNiSn) [1]. In magnetic compounds, the gap is asymmetric with regard to spin; if a full gap occurs at the Fermi energy for one spin but not for the other, the result is a half metal (ex. Co$_2$MnAl) [2]. Half-metals are important for spintronics applications such as spin transistors and non-volatile logic.

Compounds of the form A$_2$BD or A$_3$D, where A and B are transition metals and D is an $sp$ element, typically crystallize in the ternary (L2$_1$) or binary (D0$_3$) full Heusler structures, based on a bcc sublattice. These compounds are usually ferro- or ferrimagnetic, with the magnetic moment well predicted by a Slater-Pauling counting scheme, $M = Z - 24$, where $Z$ is the total number of valence electrons in the unit cell [3]. For $Z = 24$, there is no net magnetization and a gap in both the majority and minority spin DOS, resulting in a semiconducting gap (ex. pseudogap in Fe$_2$VAl) [4]. This tunability and predictability of parameters with $Z$ makes the Heusler compounds a very attractive class of materials to work with.

Cr$_2$Al (Cr$_{1.5}$Al$_{1.5}$ with $x = 0.25$) is an exception to this scheme. $Z = 21$, so according to the Slater-Pauling counting scheme it should be a metal with $M = -3$. Instead, Cr$_{1-x}$Al$_x$ is

Figure 1: Calculated Bloch spectral function of pure Cr and disordered Cr$_{0.80}$Al$_{0.20}$ alloy.
found to be antiferromagnetic for $x = 0.35$. Pure Cr is an elemental antiferromagnet with a spin-density wave that is incommensurate with the lattice. The addition of Al causes the spin-density wave to become commensurate, i.e. a simple antiferromagnetic structure, for $x \geq 0.03$. For $x = 0.15-0.26$, the Cr moment reaches $1 \mu_B$ with an extremely high Néel temperature of about 800K [5].

In the same concentration range, Cr$_{1-x}$Al$_x$ is found to be semiconducting rather than metallic. This semiconducting behavior has not yet been adequately explained by theory [6]. The gap has been estimated to be between 6-60 meV, making Cr$_{1-x}$Al$_x$ a narrow-gap semiconductor [7,8].

Electronic structure calculations were done for Cr and a random Cr$_{0.80}$Al$_{0.20}$ alloy using the AkaiKRR code, a full-potential density functional Green’s function approach based on the Korringa-Kohn-Rostoker multiple-scattering technique [9]. Disorder in alloys is treated using the coherent potential approximation (CPA) [10,11]. The generalized gradient approximation (GGA) was used to approximate the exchange-correlation energy [12], which results in equilibrium lattice constants very close to experiment [7]. For both Cr and Cr$_{0.80}$Al$_{0.20}$, a simple antiferromagnetic structure was used.

The Bloch spectral functions of Cr and Cr$_{0.80}$Al$_{0.20}$, from the electronic structure calculations, are shown in Figure 1. The Bloch spectral function is the k-projected DOS, which reduces to a single-valued function $E(k)$ (the $\mathcal{A}(E, k)$, band structure) in the case of a pure compound without disorder broadening. Figure 1 shows a significant reduction in the Fermi surface of Cr$_{0.80}$Al$_{0.20}$ compared to Cr, however it does not show a full gap.

For Cr, at the top of Figure 1, the SDW gap can be seen in the regions $\Gamma - M$ and $R - \Gamma$ [5]. States cross $E_F$ around $M$ (holes) and $X$ (electrons). Based on the Hall resistivity of Cr, conduction occurs primarily through the holes around $M$ [13]. For Cr$_{0.80}$Al$_{0.20}$, the regions $\Gamma - M$ and $R - \Gamma$ are still gapped due to the SDW. In addition, the hole band around $M$ has shifted completely below $E_F$. The electron band at $X$ still overlaps $E_F$ slightly, and disorder broadening leads to states crossing $E_F$ at several points in $k$ space. Previous Hall effect measurements of Cr$_{1-x}$Al$_x$ have shown that the conduction mechanism switches from holes in pure Cr to electrons for $x = 15$ at.% Al [7]. These calculations explain this behavior due to shifting of the hole states at M to below $E_F$.

Density functional approaches are known to severely underestimate the band gap of materials [14], and this could explain the absence of a gap in the calculated band structure of the Cr$_{0.80}$Al$_{0.20}$ alloy.

In addition, if an ordered Cr$_2$Al structure exists [15], this would decrease the disorder broadening of electron states across the Fermi energy.

Future work will investigate the possibility of an ordered structure.

References: